EXPERIMENTAL AND MODELLING STUDIES ON NEEM (AZADIRACHTA INDICA) OIL COATED UREA

Ph.D. Thesis

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EXPERIMENTAL AND MODELLING STUDIES ON NEEM (AZADIRACHTA INDICA) OIL COATED UREA

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Doctor of Philosophy

by

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ORAL DEFENCE COMMITTEE REPORT

In compliance to the letter No. **F.4(P)Ph.D./Acad./MNIT/2018-19/2259** dated **05/02/2019** the Ph.D. viva voce examination of **Shiv Om Meena (2012RCH9002)** on the Ph.D. thesis entitled "Experimental and Modelling Studies on Neem (Azadirachta Indica) Oil Coated Urea" was held on **18/02/2019** before the oral defense committee in Computer Lab at Department of Chemical Engineering at**10.30 A.M** onwards.

The following members of Oral Defense Committee (ODC) were present:

1. Prof. Shishir Sinha
2. Dr. Manish Vashishtha

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The Plagiarism report of the thesis is also examined and found to be satisfactory. The Ph.D. candidate Student **Shiv Om Meena** (**2012RCH9002**) openly defended his work before the Oral Defense Committee and successfully answered almost all the queries of the examiners.

The Oral Defense Committee (ODC), therefore recommends the award of Ph.D. (Doctor of Philosophy) of Malaviya National Institute of Technology Jaipur to Shiv Om Meena (2012RCH9002).

(Prof. Shishir Sinha)

18/2

(Dr Manish Vashishtha)

DECLARATION

I, **Shiv Om Meena**, declare that this thesis titled, **“Experimental and Modelling Studies on Neem (Azadirachta Indica) Oil Coated Urea”** and the work presented in it, are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
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- I have acknowledged all main sources of help.
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Date: 18/02/2019

Shiv Om Meena
(ID: 2012RCH9002)

CERTIFICATE

This is to certify that the thesis entitled **“Experimental and Modelling Studies on Neem (Azadirachta Indica) Oil Coated Urea”** being submitted by **Shiv Om Meena (ID: 2012RCH9002)** is a bonafied research work carried out under my supervision and guidance in fulfillment of the requirement for the award of the degree of **Doctor of Philosophy** in the **Department of Chemical Engineering,** Malaviya National Institute of Technology, Jaipur, India. The matter embodied in this thesis is original and has not been submitted to any other University or Institute for the award of any other degree.

Place: Jaipur
Date: 18/02/2019

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ABSTRACT

In order to meet the increasing global food demands enormous quantities of fertilizers are used in the agricultural sector, although this has lead to negative environmental impacts. Hence, it is imperative to develop such systems which along with ramping up the production also alleviate environmental problems and controlled release fertilizers (CRF) are one such intervention. Neem oil coated urea (NCU) is one such novel CRF which apart from meeting crop nutrient requirement during its growth phase also acts as a bio pesticide and bio insecticide.

Government of India has made it mandatory that entire quantity of indigenously produced urea and imported urea is neem coated w.e.f 1st September, 2015 and 1stDecember, 2015 respectively.

Various reserchers mainly from agriculture background have explained the importance through feild experiments of using NCU in improving production of various crops, fruits and vegetables. But no comprehensive work was done to unearth the engineering aspects of NCU.

The primary aim of the present work is to explain the physical and chemical properties of NCU which impart to it controlled release characters. Also experimental determination of nutrient release is conducted in soil and water environment to show the controlled release behaviour of NCU and its compliance with international standards for CRF. The nutrient release behaviour from NCU followed the sigmoidal release pattern as shown by other CRF but is able release the nutrient over a longer period as compared to other CRF with same core diameter and coating thickness. Also a rapid method is presented which help in verifying the controlled release charcteristics of CRF in a shorter duration .

Apart from experimental work multidiffusion mathematical model is developed for predicting the release behaviour from a perfectly coated CRF and results match well with the experimental and literature data. In order to incorporate imperfection in coating and release behaviour in soil domain a porous model is also developed. The results were matched with the results from model for perfect coating and showed an improvement in predictions. Also determination of nutrient release behaviour in soil is difficult as compared to that in water medium but the porous model presented predicted the results in soil domain accurately and can be used for other CRF also. The experimental and modelling results presented for NCU can be used for other newly developed CRF.

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ABBREVIATIONS AND NOMENCLATURE

Abbreviations

ACU	Agrium coated urea
BCU	Bentonite coated urea
BDF	Backward difference formula
BC	Boundary conditions
CEN	European Standardization Committee
CRCU	Controlled release coated urea
CRF	Controlled release fertilizers
CDU	Cyclo diurea
DAI	Days after incubation
EDX	Energy dispersive X-ray analysis
EEF	Enhanced efficiency fertilizers
ESF	Environmentally smart fertilizers
FEM	Finite element method
FTIR	Fourier Transform Infra-Red
IC	Initial conditions
IF	Intelligent fertilizers
LCU	Latex coated urea
LTPCU	Large tablet polymer coated urea
Mt	Million tons
MPO	Modified polyolefin
MPOCU	Modified polyolefin coated urea
NCU	Neem oil coated urea
NCCU	Neem cake coated urea
NICU	Nimin coated urea
N	Nitrogen
PCU	Phosphate slimes coated urea
PGR	Plant growth regulator
P	Phosphorus
K	Potassium
PU	Prilled urea
RI	Refractive Index
SEE	Standard error of the estimate
SEM	Scanning Electron Microscopy

SRF	Slow release fertilizers
SCU	Sulphur coated urea
UCU	Uncoated urea
UF	Urea formaldehyde
XRD	X-ray Diffraction

Nomenclature

ρ_{Urea}	Density of urea, g/cm^3
τ_F	Dimensionless tortuosity factor
ϕ	Liquid volume fraction,
ε	Porosity
μ	Average of coating thickness distribution, mm
σ	Standard deviation of coating thickness distribution
a	Coating thickness, mm
a_1, b_1, c_1	Constants
a_2, b_2, c_2	Constants
C_{Const} (r, t_1)	Urea concentration at the end of constant release stage, mol m^{-3}
C_{Decay} (r, t_1)	The initial urea concentration of decay release stage, mol m^{-3}
C_k	Concentration of species ‘k’ in the liquid, mole m^{-3}
C_{Sat}	Saturated concentration, mol m^{-3}
D_{eff}	Effective diffusivity, m^2 s^{-1}
D_U	Urea diffusivity in liquid, m^2/s
F_C	Weight of the neem oil coating ,g
F_i	Initial amount of NCU in the mesh bag
F_s	Weight of the NCU on the sampling date
J_{Urea}	Diffusive flux of urea, mol m^{-2} s^{-1}
M	Weight of urea sample, g
M_0	Weight of filter paper, g
M_{Core}	Mass of urea present inside the core, g
M_i	Weight of filter paper with urea sample, after evaporation, g
$M_{Release}$	Mass of urea released, g
$M_{Total\ Urea}$	Total urea mass of the NCU granule, g
N	Number of given data
N_1	Release time in hrs at 100^{o}C
N_2	Release time in days at 25˚C
N_i	Initial nitrogen content

$\%N_{NCU}$	Percent of nitrogen in the NCU
$\%NR_{C}$	Percent of nitrogen release as determined by the chemical method
$\%NR_{W}$	Percent of nitrogen release as determined by the weight method
N_s	Nitrogen content in grams of the NCU on the sampling date
$\%N_{UCU}$	Percent of nitrogen in uncoated urea
P_1	Cumulative nutrient release at 100˚C
P_2	Cumulative nutrient release at 25˚C
R_0	Core radius, mm
R_1	Water boundary, mm
R_k	Reaction rate expression for reactions in the liquid, solid, or gas phase
r_p	Particle radius of the porous (soil) medium, m
S	Specific surface of porous (soil) medium, $m^2\ m^{-3}$
S_{Core}	Surface area of urea core, m^2
S_{Diff}	Surface area of urea particle, m^2
S_k	Arbitrary source term
T_0	Lag period, s
T_1	Release time, hr
T_2	Release time, days
U, V, W	Constants
V_{Core}	Volume of urea core, m^3
Y_{Exp}	Experimental data
Y_{Simu}	Simulation results

CHAPTER 1

Introduction

Earth's population has witnessed an exponential growth in past few decades and has now reached approximately 7.0 billion and this is further expected to reach 9.5 billion by 2050 [1]. This population growth on one hand has fuelled the global food requirements and the per capita food requirement is expected to double by 2050 from the present levels [2]. On the other hand, cultivable land area is diminishing due to rapid industrialization, increasing urbanization, desertification and land degradation [3]. These intimidating factors pose a serious threat to global food security and need an immediate response and solution. Different interventions to meet the challenge of food security have already been undertaken worldwide, prominent among these is to improve efficiency of agricultural systems to produce more food from given area of land. One such intervention to meet the increasing food demands is to employ enormous quantities of fertilizers in the agricultural sector, although this has lead to negative environmental impacts. Hence, it is the need of hour to develop such systems which along with ramping up the production also alleviate environmental problems [4].

Fertilizers in broad sense are farm inputs aimed to augment the levels of available plant nutrients and/or the chemical and physical properties of soil, thereby contributing directly or indirectly in increasing the plant growth, yield, and quality.

On the basis of their chemical composition fertilizers are classified as:

1) *Mineral fertilizers* consisting of inorganic or synthetically produced organic compounds.
2) *Organic fertilizers* are waste products from animal husbandry, plant decomposition products or products from waste treatment (composted garbage, sewage sludge).
3) *Synthetic soil conditioners* are compounds whose primary function is to improve the physical characteristics of soils such as its friability, water and air transport capacity etc.

Another classification of fertilizers can be done on the basis of their nutrient content:

1) *Straight fertilizers* are those which generally contain only one primary nutrient.
2) *Compound (complex or multinutrient) fertilizers* those composed of several primary nutrients and to some extent micronutrients as well.
3) *Micronutrient fertilizers* which contain nutrients required in small quantities by plants.

Finally, fertilizers can be classified as solid or liquid fertilizers or as soil or foliar fertilizers, former being applied to soil or plant roots and the latter being applied exclusively by spraying over plant population.

1.1 Historical perspective

Mankind has been using Fertilizing substances since antiquity. The idea of applying them came from the observation in nature that plants grow better in areas marked by presence of human or animal excreta, ash residues, river mud, or dying plants. For example, fertility of river Nile mud was known to Egyptians, the Babylonians knew about importance of using the stable manure. Homer mentions about the manure in Odyssey. Pliny reports that inhabitants of north of Mainz applied “white earth,” a calcareous material as fertilizer in their fields. Romans knew about the importance of using the green manure in cultivating legumes. Towards the end of the first millenium, wood ash became one of the major fertilizers in Central Europe. However, around 1800, the plant nutrition problem became critical in most of Europe. To add to this criticality in 1798, Malthus presented the pessimistic theses, indicating that although food output could increase only in arithmetic progression but the population increase takes place in geometrical progression. Combining results of other researchers like Sprengel, Boussingault etc. with his own extensive studies, J. von Liebig presented the theoretical principles of plant nutrition and plant production in his work *Chemistry in Its Application to Agriculture and Physiology* (1840). He presented his view, although now considered obvious, that plants need some essential nutrients like nitrogen, phosphate, and potassium salts for proper growth and these are extracted by them from soil. Liebig’s *mineral theory* was augmented by experimental work of French scientist J.

B. Boussingault (1802–1887). He along with J. B. Lawes (1814–1900) and J. H. Gilbert (1827–1901) showed that inorganic nitrogenous fertilizers are helpful in plant growth. Liebig can thus be considered as the founder of the modern theory of mineral fertilizers**.** As a result of this research a number of chemical plants were commissioned in Europe to produce phosphate and potash fertilizers. Superphosphate was first manufactured in England in 1846. By the end of 19th century nitrogen demand exceeded the availability of natural fertilizers. To meet this spurt in demand an important breakthrough came with the discovery and large-scale synthesis of ammonia by Haber (1909) and its industrial realization by Bosch (1913) [5]. The development of modern fertilizers around the world can be summarized as follows: [6]

Year	**Development**
1830	First cargo of saltpeter fertilizer sent from Chile to England
1840	First cargo of Guano sent from Peru to England
1843	Manufacture of Superphosphate as the first "artificial" fertilizer, England
1860	Extraction of Potassium fertilizer from top-layer of salts of salt mines, Germany
1890	Manufacture Ammonium sulphate from coking ammonia as "artificial" N-fertilizer, Germany
1907	Production of Saltpeter fertilizer from arc-gap process, Norway
1913	Ammonia synthesis using atmospheric nitrogen by Haber-Bosch Process which became a basis for many N-fertilizers, Germany
1921	Production of Urea (carbamide) from ammonia, Germany
1929	Discovery of Ammonium nitrate as an important N-fertilizer

Almost 70 years ago, serious research began on the best nutrient forms for individual plant species under various soil and climatic conditions. Besides the classical fertilizers, other variants for example, controlled-release fertilizers, improved foliar fertilizers, nutrient chelates, and nitrification inhibitors have been developed in recent decades. This development of new nutrient forms is still in full swing in the special fertilizers sector. In the developed market economies of Western Europe, the United States, and Japan however the level of mineral fertilizer use has not been increasing since the beginning of the 1980s. In some countries genuine agricultural overproduction has occurred recently. Since better delivery of plant nutrients has led to increasing self-reliance even in third world economies (e.g., China, India, Brazil), the countries are no longer important purchasers of nutrients on the world market, so the surpluses cannot be exported without limit. The production of fertilizers is also on the increase in these countries. Thus overproduction plus regional environmental problems (nitrates entering the groundwater) are actually leading to a decrease in mineral fertilizer use in some areas. This decline will be limited by diminishing soil fertility in localities where fertility has been enhanced by decades of proper fertilization [5].

1.2 Global fertilizer consumption trends

The modern agricultural system is largely dependent on fertilizers and efficient agricultural practices are concomitant with application of fertilizers in fields. A rapidly increasing world population has made it imperative to ramp up the food production is substantially. This has in turn led to an increase in nutrient load per unit area and rapid growth of the fertilizer industry. The global demand and growth of nitrogen (N), phosphorus (P) and potash (K) fertilizers is over last ten years is outlined in table 1.1.

Table 1.1. Global fertilizer demand (million tons) [7]

Year	**N**	**P_2O_5**	**K_2O**	**Total**
2007- 2008	100.5	38.4	28.9	167.9
2008- 2009	97.7	33.7	23.4	154.8
2009-2010	101.9	37.5	23.5	162.9
2010-2011	104.1	40.5	27.6	172.2
2011-2012	108.2	41.0	27.7	177.0
2012-2013	109.8	42.2	29.4	181.4
2016-2017	114.7	45.4	32.7	192.8

However, the statistics on global use of fertilizers revels that consumption of fertilizers is highest in Asia followed by Latin and North America, whereas the consumption is showing a declining trend in Western Europe (figure 1.1). This increasing fertilizer demand and consumption pattern is the major reason behind the enhanced production and the supply of agricultural nutrients. As an indicative example world's urea producing capacity has reached 226.1 million tons (Mt) in 2016 from 44 Mt in 2011. [6]

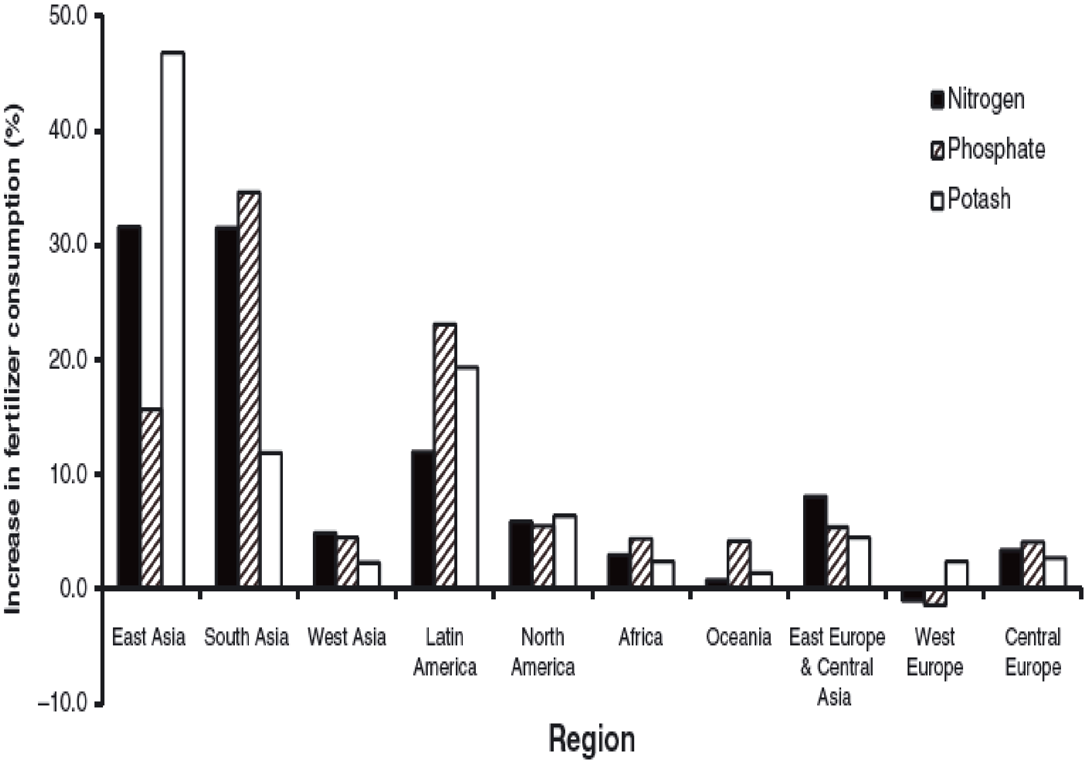


Figure 1.1. Regional contribution to change in world consumption of fertilizers, 2011–2015 [8]

1.3 Plant nutrients and their function

There is no precise definition of term plant nutrient from scientific point of view. However it will be more apt to distinguish between nutritive elements of plants and nutritive carriers. Essential *nutritive elements* for plants are those chemical elements which are needed for a normal plant life cycle and thus satisfy the following criteria:

(i) A deficiency of the particular element renders seriously affect plant growth and does not allow it to complete its life cycle.

(ii) The deficiency is element specific.

(iii) The element is a direct source of plant nutrition due to its chemical or its physical properties.

The following chemical elements fit the above criteria of nutritive elements for plants: C, H, O, N, P, S, K, Ca, Mg, Fe, Mn, Cu, Zn, Mo, B. Also other elements, such as Na, Cl, and Si, also affect plant growth positively, and for some particular plant species these elements are of great importance. Nevertheless, they do not fall in category of essential nutritive elements for plants in the strict sense of the definition. Cobalt is an element used by some bacteria, e.g., by dinitrogen-fixing bacteria and thus it also benefit plant growth though indirectly.

In general, it is not the element which itself is applied to and taken up by the plant, but plant uptake takes in form of an ion or a molecule in which the nutritive element is present, e.g., C present in CO_2, P in $H_2PO^-{}_4$,N in $NO^-{}_3$ or $NH^+{}_4$, and B in H_3BO_3. The particular molecule or ion in which the nutritive element is present is called as *nutrient carrier*. For metals, the corresponding ion or salts of ion species, e.g., K^+, Ca^{2+}, Zn^{2+}, are considered as the carrier. In this sense fertilizers acts as nutrient carriers.

Plant nutrients can be classified as, macronutrients and micronutrients. Macronutrients are those which are required by plants in high amounts and thus are present in plant tissues in higher concentrations as compared to micronutrients. Carbon, H, O, N, P, S, K, Ca, and Mg constitute the macronutrients. Rest of the nutritive elements fall in the category of micronutrients. From the viewpoint of fertilization, those nutrients which are needed by plants in large quantities and that which must be regularly supplied by fertilization are of particular interest. Basically, N, K, P, is such nutrients and to a lesser extent also Ca, Mg, and S. Calcium is a soil nutrient, which is important for an optimum soil structure. Application of micronutrients in fields is not commonly carried out, but is practiced at locations where soils are deficient in a particular micronutrient or where soils may bind this micronutrient very strongly. For instance heavy metals (Fe, Mn, Cu, Zn) and B are used in calcareous and alkaline soils (soils with a high pH value), while Mo is strongly fixed in acid soils. Acid organic soils are characterized by their low available Cu content. The plant nutrients are grouped into four groups, from a physiological point of view, as illustrated in Table 1.2.

Table 1.2. Physiological classification of plant nutritive elements, nutrient carriers, and form in which the nutrient is taken up [5]

Nutritive element	Nutrient carrier	Uptake
First group		
C	CO_2, HCO_3^-	CO_2 by leaves, HCO_3^- by roots
H	H_2O	H_2O by leaves, H_2O and HCO_3^- by roots
O	CO_2, HCO_3^-, O_2	O_2 and CO_2 by leaves, HCO_3^- and O_2 by roots
N	NH_4^+, NH_3, NO_3^-, NO_x	NH_4^+ and NO_3^- by roots, $NH_3$and NO_x by leaves
S	SO_4^{2-}, SO_2, SO_3, H_2S	SO_4^{2-} by roots, SO_2, SO_3 and H_2S by leaves
Second group		
P	$H_2PO_4^-$, HPO_4^{2-}	$H_2PO_4^-$ and HPO_4^{2-} by roots
B	H_3BO_3, borates	H_3BO_3 and $B(OH)_4^-$ by roots
Si	Silicates	$Si(OH)_4$ by roots
Third group		
K	K^+, K salts	K^+ by roots
Mg	Mg^{2+}, Mg salts	Mg^{2+} by roots
Ca	Ca^{2+}, Ca salts	Ca^{2+} by roots
Mn	Mn^{2+}, Mn salts	Mn^{2+} by roots
Fourth group		
Fe, Cu, Zn, Mo	ionic form or metal chelates, minerals containing these elements	by roots in ionic form or in the form of soluble metal chelates, Mo in the form of the molybdate

As evident from table 1.2, uptake of all the nutritive elements by plants occur in form of inorganic complexes, mostly in oxidized form or as metal ions, i.e., in forms characterized by a low energy level. Plants, particularly the green plants, meet their energy requirement by converting solar radiation energy into chemical energy. So, important plant nutrition processes are closely tied up with the unique function of plants in a greater cycle of nature, i.e., the conversion of inorganic matter into organic form. Liebig [9] thus aptly commented on plant nutrition in following way, "*Die ersten Quellen der Nahrung liefert ausschließlich die anorganische Natur*" meaning the primary source of nutrition is provided exclusively by the inorganic materials in nature.

Most of the plant organs and mainly the plant parts which are metabolically very active, like young leaves and roots, are rich in water (80–90 wt%), their organic material content is 12–18 wt% and mineral content is 2–6 wt%. Therefore, elements

C, O, H, and to some extent, N are main structural elements present in plant matter. However, they can form chemical groups e.g., carboxyl groups, amino groups, hydroxyl groups which directly participate in metabolic processes.

Many soils are deficient or have low available N, thus nitrogen is the most important fertilizer element, and its function in plant metabolism is of utmost importance. Nitrogen is an essential constituent for amino acids, proteins, nucleic acids, many coenzymes and some phytohormones. The primary biochemical processes of meristematic growth, like synthesis of proteins and nucleic acids, need N. Insufficient amounts of N, manifest itself in form of the growth rate retardations and the insufficient proteins synthesis. It is also important in chloroplasts formation, especially for the synthesis of chloroplast proteins. Hence, N deficiency leads to a low chlorophyll content; the leaves, especially the older ones becoming pale and yellow; thinning of stems and reduction in plants overall height. Abundant N supply increases the protein content (especially free amino acids) and NO_3^- content in plants. Excess nitrogen nutrition leads to luxurious plants which are frequently susceptible to fungi attack.

1.4 Nitrogen fertilizers

Nitrogen constitutes the most important nutrient for plant growth. So in present work and in many other studies word nitrogen or nutrient are used interchangeably. In general, for plants nitrogen requirement is higher than other nutrients. Nitrogen in nitrate (NO_3^-) or ammonium (NH_4^+) forms is used as nitrogen fertilizers. Ammonium sulfate ($(NH_4)_2SO_4$), ammonium nitrate (NH_4NO_3), sodium nitrate ($NaNO_3$), ammonium chlororide (NH_4Cl), and urea ($CO(NH_2)_2$) are main nitrogen fertilizers (table 1.3). Urea has highest percentage N as compared to other sources.

Table 1.3. Nitrogen content of various nitrogen fertilizers

Nitrogen fertilizer	**Nitrogen content (%)**
Ammonium sulfate ($(NH_4)_2SO_4$)	21
Ammonium nitrate (NH_4NO_3)	34
Sodium nitrate ($NaNO_3$)	16
Ammonium chloride (NH_4Cl)	26
Urea ($CO(NH_2)_2$)	46

1.4.1 Nitrogen cycle

Nitrogen is present in various forms in the nitrogen cycle existing in nature (figure 1.2). The major forms being nitrate (NO_3^-), ammonia (NH_3), ammonium (NH_4^+), organic N (organic matter) and N_2 gas. However, plants can utilize nitrogen in the form of NO_3^- and NH_4^+ only. Since nitrogen undergo change to other forms relatively easy, considerable loss of nitrogen takes place from the agricultural system. The major contribution to N loss comes from:

(i) Leaching (downward movement of NO_3^- out of the root zone)

(ii) Erosion volatilization of NH_3

(iii) Hydrolysis, denitrification (transformation of NO_3^- to N_2 gas),

(iv) Immobilization (uptake by microorganisms) and exchange (binding to soil particles) and irrigation

A reduction in the above loss of nitrogen in these plant-available forms to air, water can therefore enable crops to effectively utilize the applied fertilizer [10].

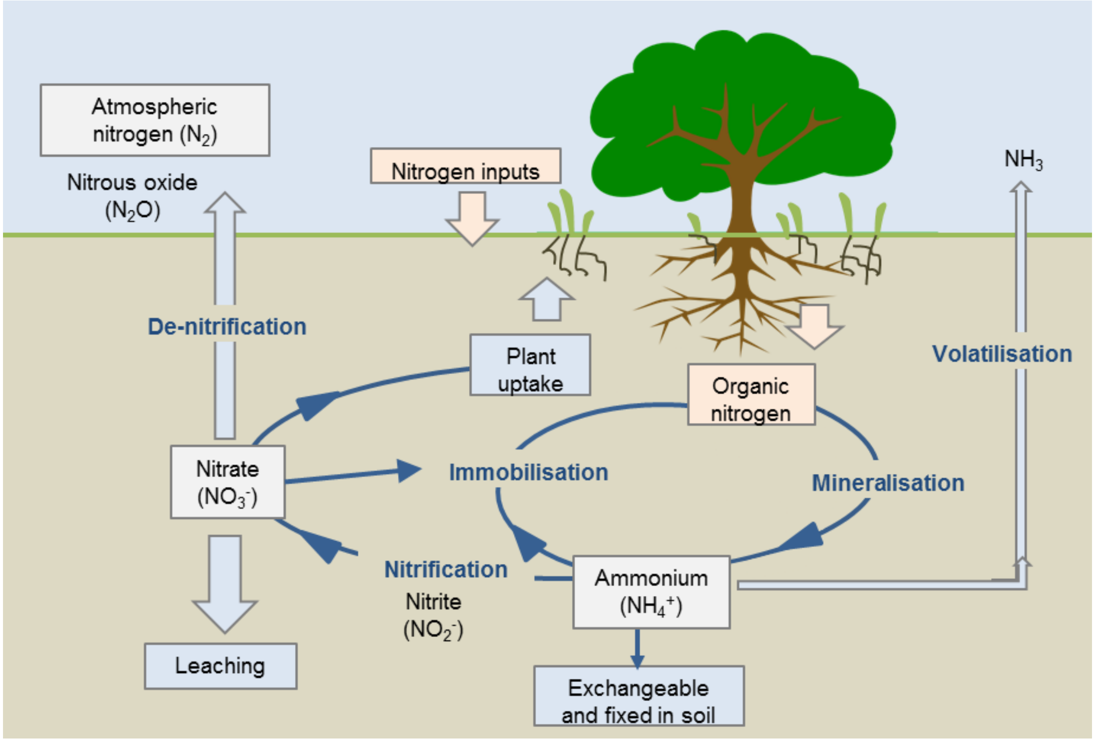


Figure 1.2. Nitrogen Cycle [10]

1.4.2 Urea

Urea (chemical formula $CO(NH_2)_2$) is the most widely used synthetic fertilizer due to its high nitrogen content (46%), low cost and ease of application. Urea has synonyms, such as Carbamide resin, isourea, Carbonyl diamide, Carbonyl diamine.

1.4.2.1 Applications of urea

Urea can be put to different uses like:

- As a fertilizer
- As a protein food supplements for ruminant
- As an ingredient in the manufacture of resins, plastics, adhesive, coatings
- Textiles anti-shrink agents and ion exchange resins
- In melamine production
- It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid and pthalocyanines

1.4.2.2 Advantages and disadvantages of using urea as a fertilizer

Application of urea as a fertilizer has following advantages and disadvantages:

Advantages:

- It has the highest nitrogen content (46%) among all commonly used N fertilizers (table 1.3)
- Production cost of urea is relatively low as it is generally associated with NH_3 manufacture.
- Can be applied to majority of crops and soil types.
- Posses ease of storage does not pose any fire risk even for long term storage
- Readily dissolves in water, leaves no salt residue after use on crops and hence can be used for foliar feeding.

Disadvantages:

- Being hygroscopic and highly soluble in water so needs better packaging quality
- Less stable as compared to other solid nitrogenous fertilizer

- It decomposes even at room temperatures that lead to losses.
- Urea containing more than 2 percent impurities cannot be used as a fertilizer, since the impurities are toxic

1.4.2.3 Nutrient release behaviour of Urea

Urea when applied to soil as a fertilizer undergoes a series of biological, chemical and physical transformations to produce plant available nutrients as shown in following steps [10].

$$(NH_2)_2CO + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3 \tag{1.1}$$

$$(NH_4)_2CO_3 + 2H^+ \xrightarrow{\text{Ammonification}} 2NH_4{}^+ + CO_2 + H_2O \tag{1.2}$$

$$2NH_4{}^+ + 3O_2 \xrightarrow{\text{Nitrosomonas/Nitrosococus Bacteria}} 2NO_2{}^- + 2H_2O + 4H^+ + \text{Energy} \tag{1.3}$$

$$2NO_2{}^- + O_2 \xrightarrow{\text{Nitrobacter Bacterium/Nitrification}} 2NO_3{}^- + \text{Energy} \tag{1.4}$$

$$NO_3{}^- \xrightarrow{\text{Microorganisms/}O_2\text{Deficient Soil}} N_2 + N_2O \tag{1.5}$$

$$NH_4{}^+ \xrightarrow{\text{Urease Enzyme/Basic Soil pH}} NH_3\ (g) + H^+ \tag{1.6}$$

It is the reactions 1.2 and 1.4 which produce required plant nutrients. Also since food requirement of plants is small during its early growth, the excess nutrients are lost in soil due to leaching. In reactions 1.5 and 1.6, the nitrogen is lost in form of hazardous gaseous emissions. The above transformations are shown in figure 1.3. Therefore, in order to minimize the losses and to increase the nutrient availability it is imperative to produce suitably modified control release coated urea (CRCU).

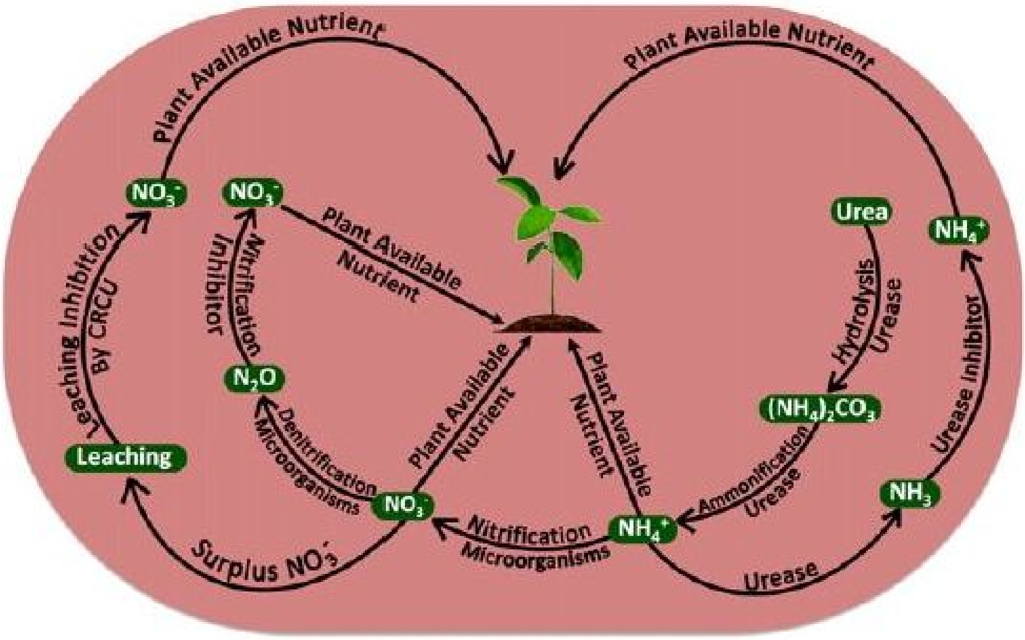


Figure 1.3. Nitrogen transformation of urea into the soil [11]

1.5 Limitations of conventional fertilizers

Various agronomical studies carried out regarding use of conventional fertilizers has revealed that only a small proportion of fertilizer, applied to the soil, is actually utilized by plants [10, 12, 13]. Also, the fertilizer application or supply of nutrients is often inconsistent with the actual plant need.

As a result of the inconsistencies, about 40–70% nitrogen, 80–90% phosphorus, and 50–70% of the total applied conventional fertilizers are lost to the environment [10, 14, 15]. These losses in agricultural nutrients not only lead to the loss of valuable resources but also cause serious environmental pollution [13]. As already explained it is the Nitrogen fertilizers which are more susceptible to losses through various routes *viz.* leaching, mineralization, erosion and denitrification processes **(**figure 1.2 and 1.3**).** The loss of phosphorus (P) occurs mainly due to surface run-off and mineralization (chemical complex formation with soil components making it unavailable for plants), whereas loss of potassium (K) is attributed to leaching and surface run-off [16, 17].

Ground water contamination by nitrates from fertilizer sources is a cause of concern to the water industry since extra cost is needed to produce potable water [18, 19]. Some other environmental concerns arising from excessive use of fertilizers includes eutrophication, blue baby syndrome, soil acidification, formation of persistent organic pollutants, accumulation of heavy metal, and adverse atmospheric effects [20]. The high water solubility potential of many fertilizers leads to osmotic stress in plant seeds and roots when applied in excess in a single dose, this ultimately causes reduction in harvest yield [12, 21, 22]. The fertilizers like urea, urea ammonium nitrate, diammonium phosphate, which form free ammonia and less water content in soil significantly increase the stress to seed and seedlings, this ultimately leads to plant injury or death [23]. Application of higher doses of fertilizers in early stages of plant growth is done with an intent to save labour costs that arise due to multiple applications (curve 3 in figure 1.4). The above mentioned facts firmly establish that the currently available conventional fertilizers are inadequate for sustainable agricultural ecosystems and require major improvements in their properties to provide better nutrient efficiency.

To overcome the shortcomings of conventional fertilizers, extensive research has been done all over the world to develop new fertilizers featuring much higher efficiency [10, 12]. *Slow or controlled release fertilizers (SRF/CRF)* are one such type of fertilizers which have been developed with an objective to retard or even control the release of the nutrients into the soil in order to accurately meet the plants nutrient demand. These new age fertilizers are usually referred to as '*enhanced efficiency fertilizers' (EEF)* as they produce at least the same or even higher harvest yield even when applied in relatively lower quantity compared to the traditional fertilizers [10]. These fertilizers are also sometimes referred to as *'environmentally smart fertilizers' (ESF)* because of their inherent ability to contain environmental pollution emanating from nutrient loss. Recently a newer and more advanced fertilizer type having tailored programmed release patterns are also made, these are referred to as *'intelligent fertilizers' (IF).*

1.6 Enhanced efficiency fertilizers

Fertilizers which offer some agronomic, economic or environmental advantages over the conventional counterparts have been described in literature as enhanced efficiency fertilizers (EEF) [10, 12, 24]. Although the concept of EEF was introduced when a slow release nitrogen product (urea formaldehyde) was patented in 1924 in Europe [25], it still remains a research topic of great interest and several researchers are working in this area. They offer nutrient delivering efficiency which is higher than conventional fertilizers. EEF are formulated in such a manner that the nutrient availability lasts for the entire crop period and hence the nutrient loss through leaching/nitrification/volatilization is substantially reduced [10, 13]. Another distinct advantage of EEF is that they help reduce the osmotic stress and burn defect in plant roots and leaves [10, 12]. EEF thus help in achieving better seasonal growth distribution and better acclimatization [12]. In addition to above benefits, EEF are more convenient to store and handle. The coating in EEF makes them less hygroscopic and hence less sensitive to the humidity present in commonly encountered storage conditions. On the other hand, conventional nitrogen fertilizers cannot be stored for longer periods of time as they are hygroscopic and thus readily absorb the atmospheric moisture and undergo caking under commonly prevailing storage conditions [26]. Synchronization of time and rate of the nutrient release to match the plant’s demand leads to a reduction and/or minimization of the loss of valuable nutrients [27]. Also the use of EEF increases the income of farmers in addition to the reduced ammonia and nitrous oxide emission [28, 29].

The mode of action of conventional and the EEF are shown in figure 1.4 which clearly depict the robustness of the latter in terms of more efficient nutrient delivery and improvement in yield and quality of agricultural products [13]. Figure 1.4, shows the relation between relative amounts of an agrochemical (e.g. urea) available as a function of time for one crop cycle. In this figure 1.4, curve 1 represents the nutrient supply patterns of a conventional fertilizer product whereas the actual plant requirement is shown by curve 2. This figure shows that during a crop cycle, the amount of fertilizer represented by the area under curve 1 is in excess, followed by the deficiency represented by the shaded area S.

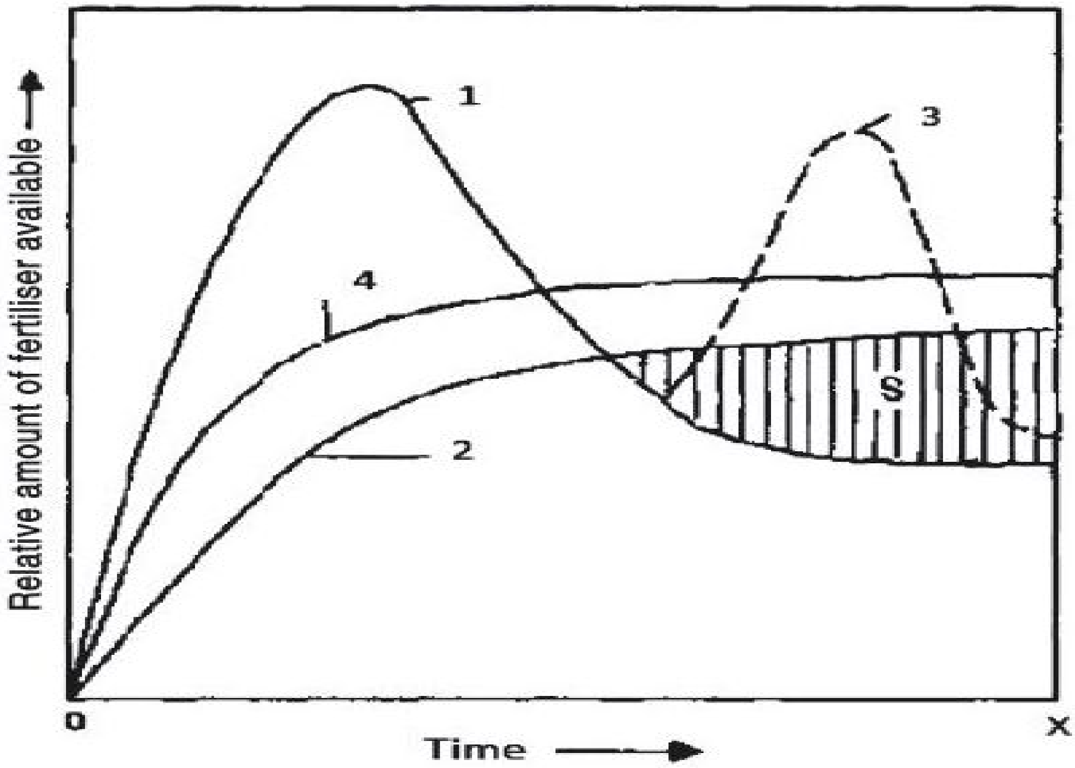


Figure 1.4. Schematic of nutrient demand and supply by a plant during its growth (OX represent one crop cycle) [13]

Therefore a crop will not receive the required amount of nutrients at right time, which ultimately leads to poor harvest yield. Curve 3 simulates the nutrient supply pattern when multiple applications of conventional fertilizers are carried out revealing two-fold loss of nutrients. However, a properly designed EEF would follow the pattern represented by curve 4. In fact, for an ideal EEF curve 4 should superimpose over curve 2 and avoid excess or deficient zones.

1.6.1 Classification of enhanced efficiency fertilizers

Based on the mode of nutrient supply and functionality, EEF are grouped into four classes:

(i) **Slow or controlled-release fertilizer:** This type of fertilizer contains plant nutrient in a form which delays its availability for plant uptake and use after its application, or which extends its availability to the plant for a significantly longer duration than a reference 'rapidly available nutrient fertilizer' like ammonium nitrate, urea, ammonium phosphate or potassium chloride. This delay in initial availability or extended time of continued availability can be achieved by a variety of mechanisms such as controlled water solubility of the material by semi-permeable coatings, occlusion, protein materials, or other chemical forms, by slow hydrolysis of water-soluble low molecular weight compounds, or by other unknown means.

(ii) Stabilized nitrogen fertilizer: In this type a nitrogen stabilizer is added. A nitrogen stabilizer is defined as a substance which when added to a fertilizer extends the time for which the nitrogen component of the fertilizer remains in the soil in the urea-N or ammoniacal-N form.

(iii) Nitrification inhibitor: A substance which inhibits the biological oxidation of ammoniacal-N to nitrate-N.

(iv) Urease inhibitor: A substance that inhibits hydrolytic action on urea by the enzyme urease. The addition of urease inhibitors to urea increases its efficiency and reduces ammonia volatilization when applied on the surface of arable land, grassland and on irrigated rice field and decreases the toxicity of urea to the seed [30].

The phytotoxicity of urea is mainly due to two factors. Firstly, the presence of transformation products (e.g. biuret) formed during the manufacturing process (heating of liquid urea above 132°C) [31]. Secondly, the breakdown products of urea such as cyanate, carbamate, ammonia and nitrites are also toxic to plants when their concentration exceeds the tolerance limit. Although modern manufacturing processes have significantly minimized the formation of biuret. However, ammonia and nitrite toxicity has not been adequately addressed [32]. Also the urea toxicity is random and unpredictable and thus application of urea in similar concentration (kg N ha^{-1}) often exhibits significantly different toxicity levels [33]. This is an indication of the fact that the concentration of urea and other fertilizers which causes toxicity depends on the plant characteristics and utmost caution must be taken when applying these fertilizers to avoid toxicity. Among the above four classes, the controlled release fertilizes (CRF) are most important and widely used EEF. A detailed discussion of these is given below.

1.7 Controlled-release fertilizers

There is no official differentiation between slow-release and controlled-release fertilizers. However, according to [12], the term controlled-release fertilizer (CRF) is used for those fertilizers in which the factors dominating the rate, pattern and duration of release are well known and controllable during CRF preparation. Slow release fertilizers (SRF) on other hand are those in which the release of the nutrient takes place at a slower rate than is usual however the rate, pattern and duration of release is nearly unpredictable and is subjected to change with changes in soil type and climatic conditions. However, in present study, we use the term “Controlled release fertilizers” (CRF) for both types *viz.* slow-release and controlled-release fertilizers

1.7.1 Classification of CRF

According to [12] CRF are classified into three major categories (figure 1.5):

(i) Organic-N low-solubility compounds

Organic compounds are further sub-divided into two types: natural organic compounds (animal manure, sewage sludge etc.) and synthetically produced organic-nitrogen, low solubility compounds. The latter category comprise of condensation products from urea and acetaldehyde. These compounds are further subdivided into biologically decomposing compounds, e.g. urea formaldehyde (UF), and chemically decomposing compounds such as isobutyledene-diurea (IBDU) or urea acetaldehyde/cyclo diurea (CDU).

(ii) Fertilizers in which a physical barrier controls the release

This category includes water soluble fertilizers in which a physical barrier is present that control the nutrient release. These are manufactured either as granules/cores coated with a hydrophobic coating, or as a matrix of active fertilizer nutrients dispersed in a continuum via hydrophobic material that retards fertilizer dissolution. However, controlled release matrices are less common compared to coated CRF. Coated granular CRF are subcategorized into those coated with organic polymer materials (e.g. thermoplastics, resins etc.) and those coated with inorganic materials (including sulfur and other minerals).

The controlled release matrix material can be either hydrophobic e.g. polyolefin, rubber etc., or gel forming polymers sometimes referred to as a hydrogels which are hydrophilic or they reduce the dissolution of the soluble fertilizer due to their high water retention (swelling).

(iii) Inorganic low-solubility compounds

Fertilizers like metal ammonium phosphates (e.g. magnesium ammonium phosphate ($MgNH_4PO_4$)), and partially acidulated phosphate rock (PAPR) belong to this category.

The biologically and microbially decomposable N products, like UF, are commonly referred to in the trade as SRF and coated or encapsulated/occluded products as CRF.

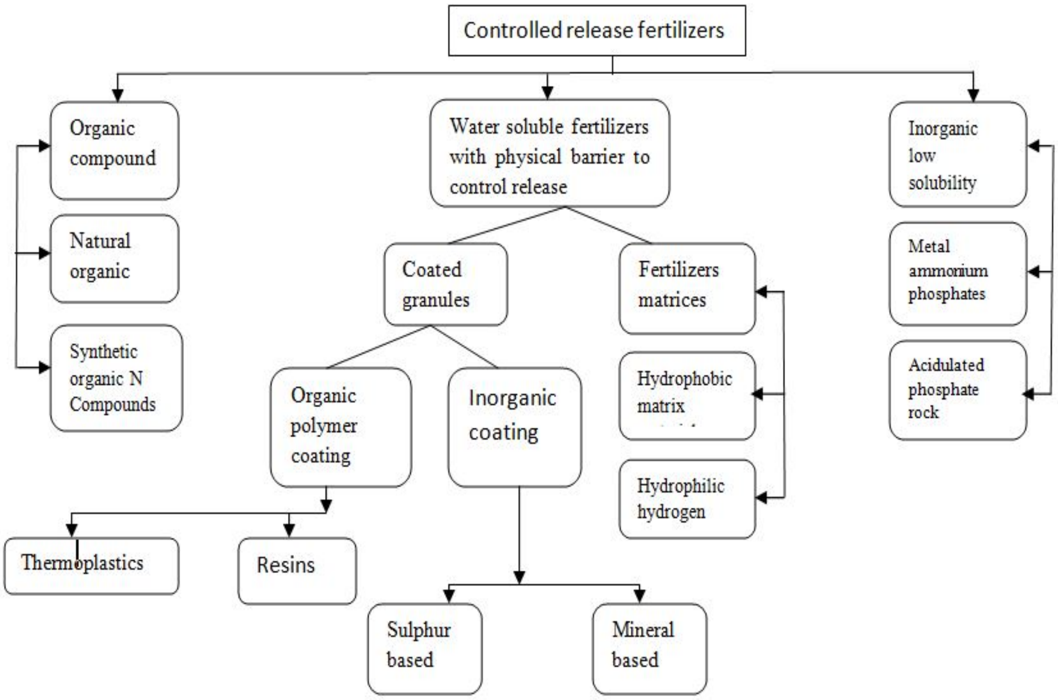


Figure 1.5. Classification of CRF

1.7.2 Standards for CRF

The European Standardization Committee (CEN) task Force on CRF has given following terminology and criterion for characterization and standardization of CRF [34]:

(i) *Release:* It refers to the transformation of a chemical substance into a plant-available form (e.g. dissolution, hydrolysis, degradation, etc.);

(ii) *Controlled /Slow release:* The nutrient release rate from the fertilizer must be slower than that from a fertilizer in which the nutrient is readily available for plant uptake. For example, for a slow-release nitrogen fertilizer, the release rate/plant response must be less than that from an application of urea, or ammonium or nitrate solution;

(iii) *Declaration:* A fertilizer may be described as CRF if the nutrient or nutrients declared as slow-release meet, following three criteria (at a temperature of 25^{o}C):

(A) No more than 15% released in 24 hrs,
(B) No more than 75% released in 28 days,
(C) At least about 75% released at the stated release time.

1.7.3 Characteristics of CRF

Apart from competition between soil and plant roots for available nutrients in the soil-plant system, there exist complex interactions between plant roots and soil micro-organisms such as chemical and physical reactions on and within soil particles and soil conditions conducive to losses of plant nutrients that affect nutrient availability. Majority of transformations which nutrients undergo in the soil/soil solution are concentration dependent [35]. Any surplus amount of plant nutrients in the soil which is not taken up by plants can follow three types of pathways that eventually decrease their availability to plants [35]. These are:

(i) Microbial (nitrification, denitrification, immobilization);
(ii) Chemical (exchange, fixation, precipitation, hydrolysis);
(iii) Physical (leaching, run-off, volatilization)

The cardinal principle to be followed in any application of plant nutrients (through fertilizers) should always aim to avoid a surplus of plant-available nutrients in the soil. This in turn will increase nutrient-use efficiency and also minimize harmful effects on the environment. Since the root system of most of the arable crops only explores 20-25% of the available soil volume in any one year. Therefore, the quantity of plant available nutrients in soil will be influenced not only by the stage of plant growth and nutrient demand, but also by the rate of delivery of plant nutrients to the root system through mass flow and diffusion. The single application of conventional N fertilizers (curve 1 figure 1.4) results in excess of fertilizer in the early growth stages and deficit at later stages. Matching nutrient demand with the fertilizer availability is shown diagrammatically in figure 1.6 [27]. In case of phosphate (P) and, to a lesser extent, in potash (K) fertilizers any excess nutrients may remain in the soil for the next crop. However for N fertilizers any surplus remaining in soil at harvest is likely to be lost by leaching and denitrification.

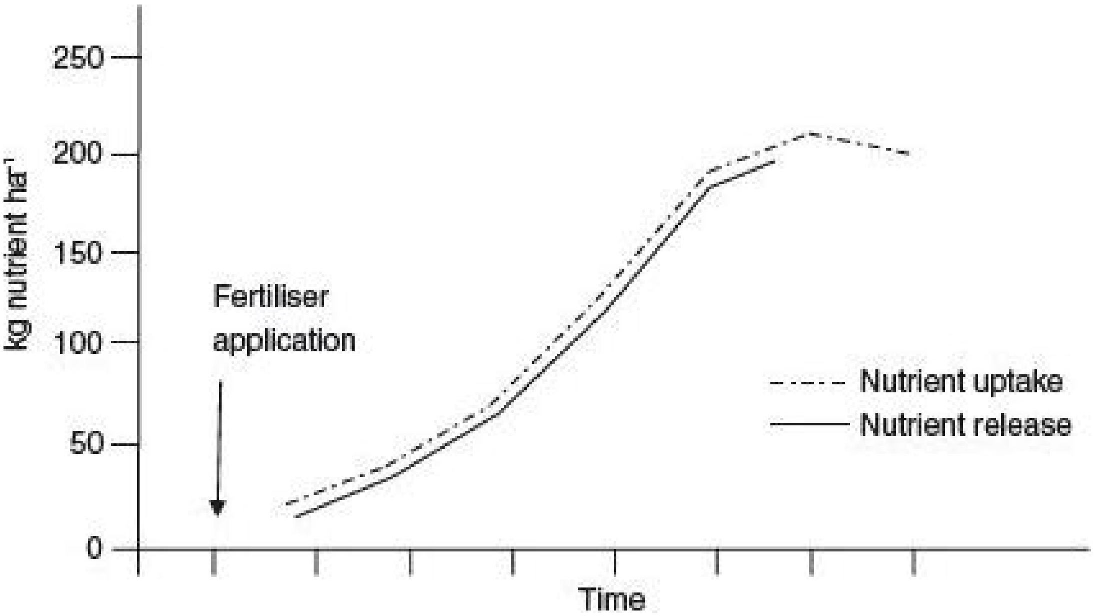


Figure 1.6. Concept of an ideal fertilizer (the nutrient release is synchronized with the crop's nutrient requirements) [36]

From figure 1.6, it can be inferred that an ideal fertilizer should release nutrients in a sigmoidal pattern for optimal plant nutrition uptake and consequent reduction in nutrient losses by processes that compete with the plant's nutrient requirements.

A sigmoidal pattern of nutrient supply from fertilizer can be obtained by applying so-called 'enhanced-efficiency fertilization concept' which implies applying N fertilizer during plant growth in several split applications (figure 1.7) [27].

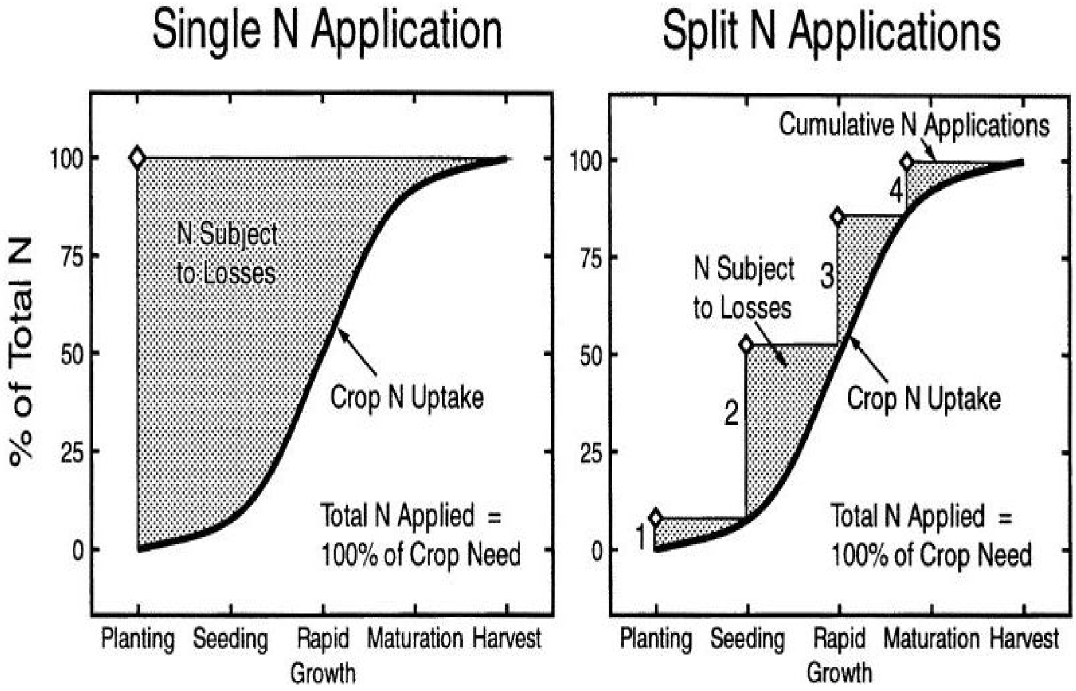


Figure 1.7. Enhanced-efficiency fertilization concept [36]

In figure 1.7, potential N losses occurring when N fertilizer is applied in a single application as compared to split applications is also depicted. Although split application may lead to a reduction in total N losses as compared to single application but still the overall efficiency is much lower than that achieved by using EEF in general and CRF in particular.

Undoubtedly, intensive farming systems (e.g. in European countries) using the enhanced-efficiency fertilization concept, can achieve high nutrient/ nitrogen use efficiency, thus reducing any negative environmental impact. The cost of applying N in split application rates may be comparable or even more profitable than where the EEF are used. However, there are some obvious drawbacks to using a split application system, like it is more labour-intensive, it requires extra fertilizer application which also involve an energy cost, it reduces on-farm labour flexibility, is mainly dependent on weather and field conditions, movement in the field may be restricted or impossible, and also there is the risk of missing the 'window of opportunity for fertilizer application' [37]. Thus to achieve better farm management farmers now a day's prefer one application of CRF instead of several split applications of conventional fertilizers.

CRF can achieve better synchronization between nutrient supply and uptake. However, in order to identify the 'optimum' CRF, it is necessary to predict the rate of nutrient release. The temporal release pattern from coated fertilizers ranges from parabolic release (with or without 'burst'), to linear release, to sigmoidal release as shown in figure 1.8.

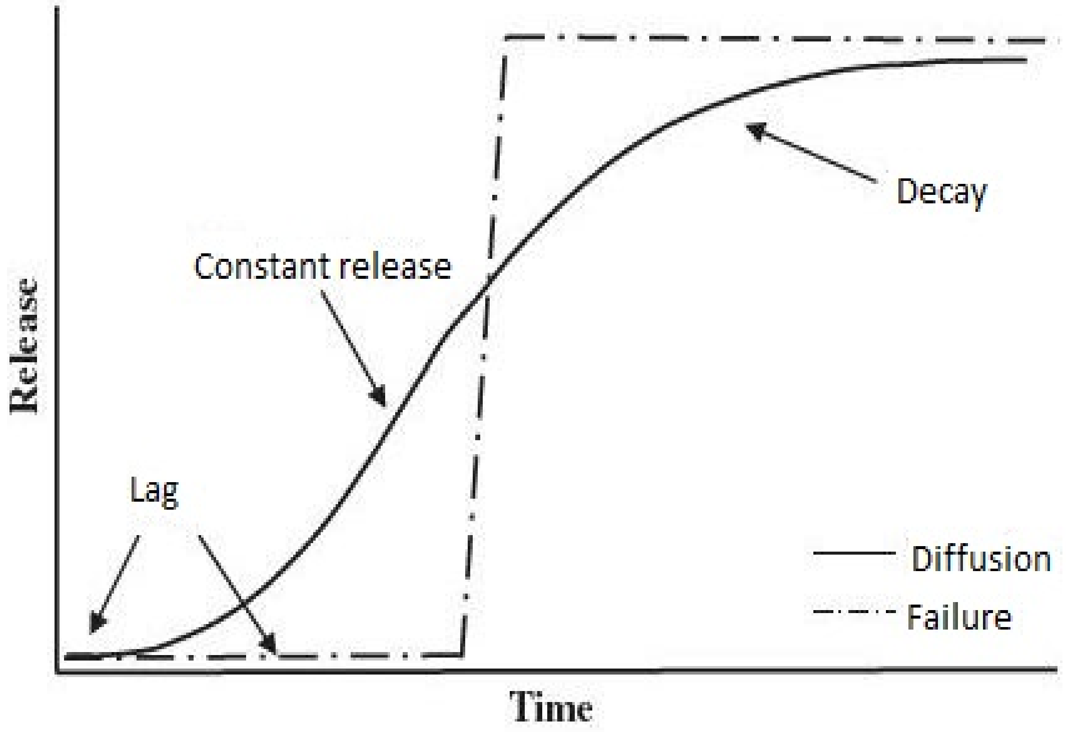


Figure 1.8. Temporal Release from a single coated urea granule: diffusion vs. failure. Failure means the complete absence of slow-release [35]

The linear and sigmoidal release patterns show better matching with nutrient uptake by plants than does the parabolic release [35, 38, 39]. In sigmoidal release pattern the release of nutrients begins only after a certain lag time, i.e. some days after application. Afterwards, it is preceded by constant release and decay stages (figure 1.8). Nutrient release from sulphur-coated urea (SCU) usually shows a parabolic pattern. However, presence of cracks in the coating of a SCU will lead to an immediate release of one third or more of its urea sometimes denoted as ‘burst’, when it comes into contact with water and about one third of the urea may be released long after it is required by the plant (the ‘lock-off’ effect) [35, 39, 40, 41]. To improve the mechanical strength and attrition resistance of SCU, it is preferable to do a double coating with sulphur and a polymer [42].

1.7.4 Mechanism of controlled release

In order to measure the effectiveness of a CRF, is important to understand the mechanism of controlled release. Generally, an accurate understanding of the controlled release mechanism is difficult since it depends on a number of factors like the nature of the coating material, the type of CRF, prevailing agronomic conditions and many more. A number of different mechanisms are cited in the literature and these are still under development. Liu [43] and Shaviv [35] proposed a release mechanism for CRF based on multi-stage diffusion process. According to multi diffusion model, after the application of CRF in soil, the irrigation water penetrates the coating to condense on the solid fertilizer core; this is followed by partial nutrient dissolution (figure 1.9).

This leads to development of an osmotic pressure within the containment; as a result of this the granule consequently swells and can follow two pathways. In the first case, when osmotic pressure overcomes the threshold membrane resistance, the coating bursts and this leads to a spontaneous release of entire core material. This is generally called as the “failure mechanism” or “catastrophic release”. In the second case, if the membrane is able to withstand the developing pressure, the core fertilizer material is released slowly through diffusion for which the driving force may be a concentration or pressure gradient, or combination of both, this is called as “diffusion mechanism”. The failure mechanism generally occurs in frail coatings (e.g. sulfur or modified sulfur), while polymer coatings (e.g. polyolefin) or neem oil coatings are exhibit the diffusion release mechanism.

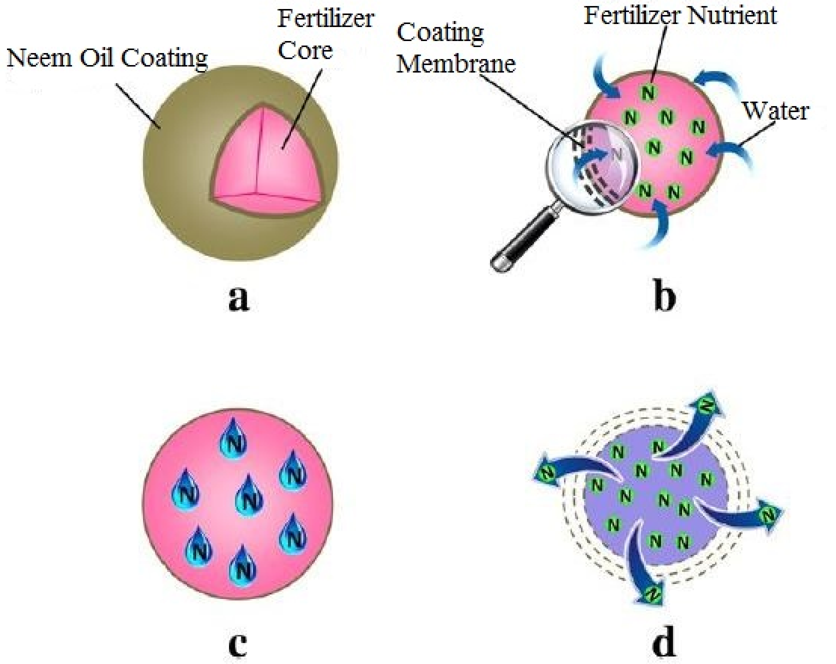


Figure 1.9. Diffusion mechanism of controlled release; (a) Fertilizer core with neem coating, (b) Water penetration into the coating and core granule, (c) Fertilizer dissolution and osmotic pressure development, (d) Controlled release of nutrient through coating membrane

The controlled release of nutrients is also governed by other factors like ambient temperature and moisture, the release rate is higher at higher temperatures and moisture content [44]. The CRF release mechanism is basically a nutrient transfer from the fertilizer-coating interface to the coating-soil interface, driven by water. The governing parameters for this release mechanism are: (i) diffusion/swelling; (ii) degradation of the coating, and (iii) fracture /dissolution.

1.7.5 Stages of nutrient release from CRF

The nutrient release behavior from CRF in soil and water environment (figure 1.9) shows the following stages:

1. **Lag stage:** In this stage mainly the water vapor penetrates into the granule and hence dissolves a small fraction of solid fertilizer. The driving force for this movement of water vapor is provided by the vapor pressure gradient across the coating. Condensed vapor can occupy the small volume provided by the voids inside the solid core and those present between the core and the coating. The lag period can

be explained as the time needed to fill the internal voids of the granule with a critical volume of water. Alternatively, the lag period can be ascribed to the time which is needed for the establishment of a steady state between the flux of water entering the granule and the flux of solute leaving it. Once a steady state is established the volume change in case of granule is negligible. In the terminology of irreversible thermodynamics the system can be described as one with zero “net volume flux”.

2. **Constant release stage:** The second stage called as the constant release stage, begins when a critical volume of saturated solution accumulates inside the granule. The nutrient release rate remains constant as long as the saturated solution inside the granule is in equilibrium with the non dissolved solid fertilizer. This constant saturation concentration provides the constant driving force required for the fertilizer transport since the concentration of the fertilizer in the external solution is almost negligible.

3. **Decay stage:** As time proceeds, the complete dissolution of the solid fertilizer inside the core leads to a decrease in the concentration of the internal solution; this decrease is due to the continuing concomitant fluxes of nutrient being released out and water flowing into the granule. Therefore, the driving force for the release decreases and the release rate decays. This third stage of the release is aptly called the “decay stage”.

1.7.6 Advantages and disadvantages of CRF

The advantages and disadvantages of using CRF can be summarized as follows:

Advantages

- CRF improve the uptake of nutrients by plants through synchronized (preferably sigmoidal) nutrient release, and significantly reduce possible losses of nutrients, such as nitrate by leaching and ammonia through volatilization Their use also lead to a reduction in N_2O emissions. This in totality leads to a reduction in environmental pollution
- CRF usage results in savings in fertilizer quantity, time energy and labor cost because only a single application is required for the crop cycle.

- Application of CRF reduce toxicity, particularly to seedlings, which result from the application of soluble conventional fertilizers due to high ion concentrations leading to osmotic stress and specific damage to plants at different growth stages. They also reduce lodging and injury from ammonium ions. CRF use also inhibits leaf burning, dermal irritation, and inhalation problems (figure 1.10). Additionally, they improve soil quality, handling properties and germination rates.
- A reasonably good prediction of nutrient release can be achieved using CRF coated with hydrophobic materials such as polymer-coated fertilizers since they are less sensitive to soil and climatic conditions. Their linear or sigmoidal release comply well (within certain limits) with the plant's nutrient requirements. Thus, they can positively contribute to advanced fertilizer management programmes and to innovative, high technology farming systems such as no-till farming with single *co-situ* fertilizer application [22].

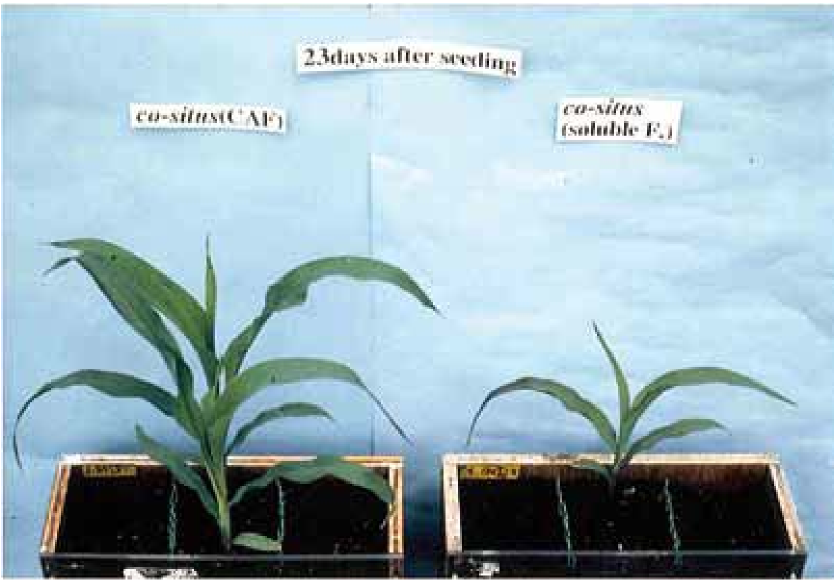


Figure 1.10. Comparison of growth of maize plants fertilized with polyolefin coated urea (left) with a conventional uncoated urea (right). The maize plant fertilized with the conventional fertilizer shows serious salt injury [34]

- The efficient predictions about long-term nutrient release from some types of CRF make it possible to develop software programs for their use on different crops and with varying soil types and agronomic conditions. Such software programmes can be very reliable particularly for polymer-coated CRF since for these there is a reasonable good correlation between temperature, release of nutrients and plant growth [35].

Disadvantages

- CRF are expensive and pose marketing issues. The manufacturing cost of most of the CRF is considerably greater than that of conventional synthetic fertilizers. The high cost is due to the fact that firstly, CRF have to go through complicated production processes, secondly, to achieve a perfect coating producers usually employ size separation of raw granular materials which makes the product more expensive, and thirdly in most cases the coating material is several times greater in price than the fertilizer material itself. Also CRF require improved marketing through specialized advisory services and sales expertise compared to conventional fertilizers, this high cost factor coupled with marketing issues is preventing their wide use in mainstream agriculture.
- Furthermore, some of the coating materials used to produce CRF are non-biodegradable and are toxic to the soil.
- Some CRF also drastically change the soil's pH, which is undesirable for example when large amounts of SCU are applied, both sulphur and urea contribute to increase soil acidity.
- Since no standardized methods exists for reliable determination of the nutrient release pattern from CRF. So in most cases, the release pattern of CRF is uncertain in field applications. The field application of CRF is also affected by a lack of data pertaining to the release kinetics in various types of soil and environmental conditions of interest to the agriculture industry. CRF that are currently used are also vulnerable to changes in temperature, ambient moisture, bioactivity of the soil, and wetting and drying cycles of the soil. Variations in any of these conditions will render the release rate unpredictable and will thus negatively impact the nutrient release efficiency, especially if the release rate has been calibrated for a specific kind of crop. In addition, CRF do not respond directly to the plant's nutrient demand for nutrients but release nutrients at a constant rate regardless of the fact that whether a plant is demanding more nutrients or none at all [35, 43-46].

1.8 Neem oil coated urea (NC U) and its benefits

Neem, *Azadirachta indica* plant is native to the arid regions of the Indian sub continent, where it grows to 12-24 m high. It can be propagated easily by seed, or 9 to 12 month-old saplings can also be transplanted. Fresh fruit yield per neem tree ranges between 37 and 50 kg per year. Forty kg fruit yields nearly 24 kg of dry fruit (60%), which in turn gives 11.52 kg of pulp (48%), 1.1 kg of seed coat (4.5%), 1 kg of husk (25%) and 5.5 kg of kernel (23%). The kernel gives about 2.5 kg of neem oil (45%) and 3.0 kg of neem cake (55%).

Figure 1.11. Tree of Neem (Azadirachta indica)

Neem oil extracted from the seeds of the neem tree has insecticidal and medicinal properties due to which it has been widely used in pest control. Neem oil is obtained by crushing of seed (Kernel) using either cold pressing or by a process incorporating temperature control. Neem oil can also be obtained by solvent extraction of the Neem seed, fruit oil, cake or Kernel. It is yellow to brown in colour, having a bitter taste, and a garlic/sulfur like smell. Neem oil apart from being used in urea coating can is also used in many other products (like toothpaste, cosmetics, soaps, and pet shampoos) these days.

The cake left after oil extraction is generally used as manure and also for making neem cake coated urea (NCCU). The various neem products are shown in figure 1.12.

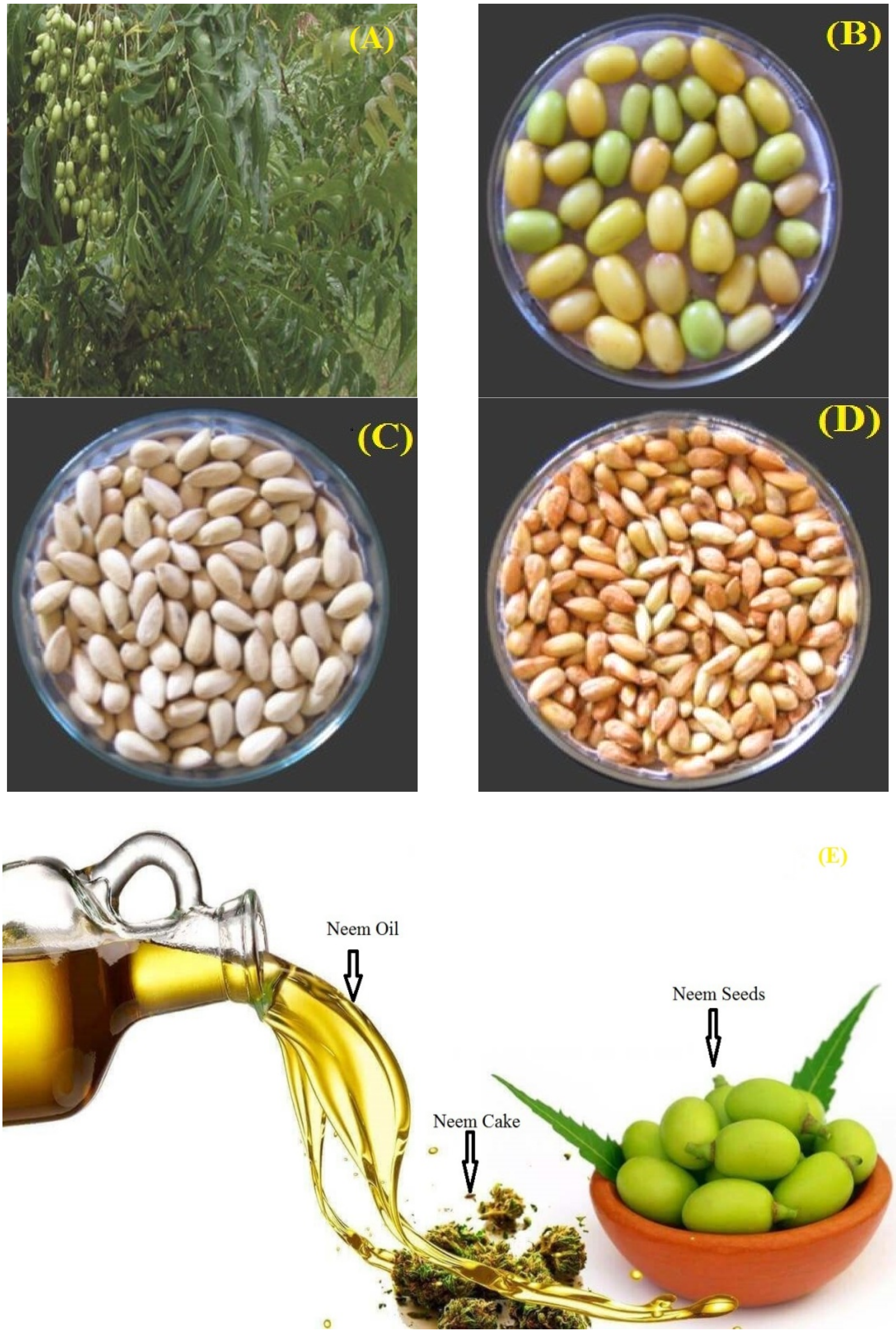


Figure 1.12. (A) Part of Neem tree bearing fruit. Neem Products: (B) Fruits, (C) Seeds (with endocarp), (D) Seeds (without endocarp), (E) Neem oil

Initially, during 1990’s it was suggested that the press cake left after the production of neem oil has a controlled-release and nitrification inhibiting effect, aside from other possible uses. It was therefore recommended to add neem cake to urea to form neem cake coated urea (NCCU) or nimin coated urea (NICU) (nimin is an extract from neem cake) to improve nitrogen use efficiency and to reduce losses [47]. Also various Indian agricultural scientists [48-53] obtained encouraging results when using NCCU in place of conventional prilled urea for rice. However the use of NCCU or NICU was apparently not practiced on a large scale by farmer community, neither in India where the tree originates, nor in other tropical countries to which it has been brought in the past. The main reason was difficulty in procuring sufficient quantities of neem cake at the village level, the additional labour needed for blending and non availability of mechanical process for blending. Whatever the reason, no attempt has been made to develop the technology to coat urea with neem on a wider commercial scale [54] and hence no industrial scale production of these neem based CRF was attempted by fertilizer manufacturers.

However, last 8-10 years has witnessed a renewed interest in using the neem based products in agricultural sector particularly in India. Among these NCU is fast emerging as an important CRF because of its multiple benefits. Neem oil contains melicians (generally known as neem bitters) of which Epinimbin, Deacetyl, Salanin and Azadirachtin are the active fractions, which showed dose dependent nitrification inhibition action [55]. When NCU is applied to soil, the Neem Triterpenes inhibit the activity of nitrifying bacteria which results in delayed transformation of ammonical nitrogen into nitrite nitrogen. This leads to substantial reduction in the loss of fertilizer and pollution of groundwater. NCU also ensures slow and continuous availability of nitrogen/nutrient throughout the crop growth, nourishing the saplings for a longer period, and thus avoiding the repeated use of fertilizer. Other potential benefits of using NCU includes, increase in crop yield, efficient pest control management leading to savings, increases in the shelf life of the product and preventing urea misuse as feedstock for other chemical industry. Thus NCU offer a lot of advantageous features as expected of a CRF.

Also being biodegradable and organic in nature it overcome the shortcomings offered by polymer/inorganic material coated CRF as explained before. The cost of NCU is only 3-4% higher than uncoated urea (UCU), so it is even cost effective.

In summary, the **advantages** of the Neem coated urea can be enumerated as follows:

- In context of India, even a conservative saving of 10% of the urea loss due to Neem oil coating would amount to about saving of 2 million tons of urea or a reduction in subsidy component to the tune of Rs. 1,700 crores per annum considering total subsidy on urea to be Rs. 18,000 crores per annum)
- The use of NCU leads to a proportional saving in consumption of naphtha or natural gas.
- Increased crop yields due to effective nitrogen utilization emanating from controlled release characteristic of NCU.
- Reduction in ground water and soil pollution levels as NCU inhibits leaching of nitrates and gaseous emissions.
- It provides an opportunity for entrepreneurs to commercialize local available Neem oil and supply it to fertilizer unit.
- Development of Small Scale Industries in rural areas leading to employment generation.

1.8.1 Government of India policy on NCU

Looking at the positive aspects of NCU and its role in efficient agriculture management Government of India, on 2nd June 2008, notified the policy for encouraging production and availability of fortified and coated fertilizers in the country wherein the indigenous manufacturers/producers of the subsidized fertilizers were allowed to produce fortified/coated subsidized fertilizers up to a maximum of 20% of their total production of respective subsidized fertilizers. This ceiling of production of NCU was increased in stepped manner, on 11th January 2011, the ceiling of production of NCU has been increased from 20% to a maximum of 35% of their total production of subsidized fertilizers and on 25th May 2015, Department of Fertilizers made it mandatory for all the domestic producers of urea to produce 100% urea as NCU. Entire quantity of indigenously produced urea and imported urea is being neem coated w.e.f 1st September, 2015 and 1stDecember, 2015 respectively in India [56].

1.9 Scope and objectives

Most of the work reported in literature on NCU is mainly confined to elucidate its effect on increasing the crop yield and plant growth [57-61]. However, literature lacks any comprehenshive study on NCU as a CRF, covering major aspects such as its charcterization, determination of nutrient release rate, comaprison with other CRF and model devlopment to predict the release rate under various conditions. The present thesis is an attempt to fill this gap in scientific knowledge about NCU that exist.

The present thesis focuses on experimental and the modelling aspects of nutrient release from NCU. The major objectives of this research are to study the fundamentals of CRF, mechanism of controlled release, experimental determination of nutrient release from NCU in water and soil environment, its behaviour and suitability as CRF, its comparison with other CRF, mathematical modelling of nutrient release from NCU with an aim to unearth the stages of nutrient release as seen in other CRF. The specific objectives of present work are as follows:

1. Preparation of NCU and its Characterization using various analytical tools.
2. Experimental determination of nutrient release from NCU in soil and water domain.
3. Comparison of experimental release rate of NCU with other CRF.
4. Development of a rapid technique for experimental determination of nutrient release from NCU
5. Mathematical model development and determination of nutrient release from single NCU particle with perfect and imperfect coating for nutrient release in water and soil domain. Model validation done from experimental and literature data.

1.10 Thesis structure

The work conducted as part of this thesis has been reported in form of the following chapters.

Chapter 1

The chapter gives an overview about fertilizers, plant nutrients, CRF and NCU with focus on the research objectives of this study.

Chapter 2

In this chapter, the literature review of controlled release coated urea (CRCU) products is presented. Major focus is on the coating materials, coating methods, release experiments and a critical analysis of the controlled release mechanism for CRCU. To enhance the understanding of the subject, chapter has been divided into sections according to types of coating materials used to produce CRCU.

Chapter 3

In this chapter, preparation of NCU along with physical and chemical characterization is explained. Experimental determination of nutrient release behaviour in water and soil domain, along with a rapid technique needed to verify the label specifications of nutrient release rate and duration is also included in the chapter. To establish the superior behaviour of NCU as a CRF the results are compared with literature data of other CRF.

Chapter 4

In this chapter, multi diffusion model is developed for multilayer to predict nutrient release from NCU unveiling the three stages of nutrient release as explained in literature for other CRF. The model was also validated with experimental results for CRCU coated with other materials differing from NCU in core and coating thickness. Also effect of varying core and coating thickness on nutrient release behaviour is explained.

Chapter 5

The chapter presents the porous model for nutrient release with an imperfect coating thickness in water and soil environments. In addition, it is compared to our previous model for perfect coating model and shows an enhancement in its predictive ability because the imperfection of the coating layer has been integrated in the model. On the basis of the proposed model, the influence of coating variation and soil types on nutrient release behaviour are also investigated

Chapter 6

This chapter concludes the thesis with emphasis on the discussion based on the experimental, modelling and simulation results of the previous chapters. It also focuses on the recommendations related to future work based on the new gaps found in previous chapters.

The thesis ends with references used in present work and a brief biodata of author is given.

CHAPTER 2

Literature Review

Although extensive literature is available on CRF, however a comprehensive literature review of controlled release coated urea (CRCU) products is still not available. The present chapter is an attempt to elaborate the existing knowledge pertaining to CRCU. The major focus of present chapter is to deal with coating materials, coating methods, release experiments and a critical analysis of the controlled release mechanism for CRCU. However the literature review presented here is related mainly to contemporary and 21st century research in the area of interest. Although to link the present state of knowledge with the historical evolution of CRCU, some classical papers are also included.

The present chapter is divided into various sections according to types of coating materials used to produce controlled release coated urea (CRCU).

2.1 CRCU from sulfur based coating materials

Sulfur was the first material to be used for urea coating as it offers various advantages. The initial significant work on urea coating was done by Blouin et al. [62] for the Tennessee Valley Authority (TVA), USA. They provided a cost effective and simple production process for the coating of urea with sulfur in order to impart it a controlled release characteristic. Initially, urea granules were impregnated by a petroleum by-product (e.g. petrolatum, motor oil, soft wax, etc.) to act as an impervious sealant and sub-coating. A vacuum was then applied to cause the sealant material to penetrate the granules more thoroughly. The sealant was considered an immobile component that prohibited urea dissolution by filling small channels via capillary action. In turn, the urea was tumbled in a second rolling drum and spray-coated with molten sulfur. Finally, the sulfur coated urea (SCU) was subjected to a third compartment wherein plasticizers (e.g. polyethylene or polyvinyl acetate) adhered to the sulfur shell to aid the spreading and fusion of the sulfur layer and decrease crack formation. For some products, the addition of a plasticizer was proposed as a substitute using inexpensive, finely divided powders (for example, talc or vermiculite) to render a uniform sulfur layer and decrease the incidence of layer cracking. To achieve a comparative study, urea was coated with petrolatum-only or sulfur-only. A 24-hour dissolution test in water was done to evaluate coating effectiveness. The authors found that the oil-only coating was absolutely ineffective to withstand water permeability. The sulfur-only coating was mildly effective, whereas a combination of both gave effective controlled release results. The coating shell with an oil to sulfur ratio of 3:21 withstood water the most with only 1% dissolution in 24 hr. Despite the controlled release advantages, this study still had a challenge to address. The presence of the sealant sub-coating could not negate the need for a uniform sulfur coating. If the sulfur coating was not sufficiently uniform to avoid fissuring, the urea substrate dissolved within minutes, even in the presence of the sealant sub-coating.

In 1968, Rindt [63] reported that the addition of plasticizers moderately reduced the water permeability of the sulfur coating and that the sulfur solidification period was extended while its tackiness was worsened by plasticizers. This problem was addressed by applying a microcrystalline wax coupled to micro biocides. This involved a three step process by which molten sulfur was initially sprayed on a rolling bed of urea granules in an undulating drum, after which molten wax was poured on the sulfur coated granules. They believed that the wax coating was subject to attack by soil microorganisms. Hence, 0.5–2% of micro biocides (e.g. pentachlorophenol or coal tar) was added to the wax to combat bacterial attack. Lastly, in order to enhance flow while avoiding tackiness from the wax, a conditioner was dusted onto the cooled coated granules. The addition of about 1% diatomaceous earth (kaoline clay or vermiculite) was used for this purpose. Twenty-four hour and longer dissolution tests revealed dissolution rates of 3.5–42% and 0.8–1.1%, respectively. The higher dissolution rate for the 24 hrs trial was attributed to smaller particle size.

The aforementioned work was up-scaled to plant capacity (300 lb/hr) by the same authors [45]. They applied the same technique for coating and dissolution study that focused on evaluating optimal parameters for a more effective sulfur coating. It was found that coating thickness was reciprocal to dissolution rate. Urea particle size distribution also had an inverse effect; i.e. smaller granules dissolved earlier than larger counterparts. The higher dissolution of small particles was due to granule sphericity as the surface to volume ratio of smaller spheres is greater compared to larger spheres. Therefore, with an equal amount of coating material applied to both small and large granules, smaller granules received thinner coating which then granted quicker dissolution. The effect of higher air pressure permitted a finer coating which also enhanced dissolution rates. As for coating effectiveness, their 'seven day dissolution test' became a reference point thereafter for other researchers. This test measured the amount of urea released by a 250 g coated sample immersed in 250 ml of water at 100°F for seven days.

Another study by Tsai [64] at the University of British Columbia, aimed to develop a process for coating urea with sulfur using a spouted fluidized bed. A 'sulfur-only' coating was applied and optimal process conditions were evaluated to attain reasonably controlled release characteristics. Urea was coated with molten sulfur concurrently with fluidizing air in a spouted bed under certain conditions of temperature and pressure. Optimized conditions included operating temperature of 80°C, fluidizing air flow at 0.65m^3/min, and pressurized atomizing air at 208 kPa. Their seven-day trial found 30% urea dissolution. Similar to Tsai in 1997 Choi [65] also studied urea coating with sulfur and derived parameters that predominantly affected the coating performance of a spouted bed. Urea coating with molten sulfur was carried out in batch as well as continuous operations and then followed by the seven-day dissolution test. Nitrogen pressurized molten sulfur was introduced with pre-heated atomizing air at the base of the spouted bed and sprayed onto the urea fluidized bed concurrently followed by drying and withdrawal. He recommended a spray angle of forty degrees and the use of multiple spouted beds as well as an extended coating period for better results in terms of coating uniformity, which directly affects the controlled release characteristics of coated urea. The TVA dissolution test findings saw a minimal dissolution of 32.8% at seven days.

Ayub [66] prepared sulfur coated urea in a 2-D spouted bed and evaluated the effects of spouting air temperature, atomizing air and liquefied sulfur flow rates on the quality of sulfur coated urea in terms of the dissolution rate. It was found that the dissolution rate was a function of spouting air temperature but the rate remained unaffected by the atomizing air flow rate. For example, dissolution was 100% and 95.61% at spouting air temperatures of 69°C and 82.5°C at atomizing air flow rates of 1.0 and 1.4 m^3/hr, respectively. The major dependence of coating quality on spouting air temperature was determined in terms of sulfur's behavior at different temperatures. At lower spouting air temperatures, the exterior of the sulfur particles solidified prior to coating the urea's surface. To the contrary, sulfur particles close to melting point solidified after coating the urea granules resulting in a more uniform coating layer. The seven-day dissolution trial resulted in a minimal level of 95.61% at the highest spouting air temperature (82.5°C), with a sulfur flow rate of 33.9 g/min and atomizing air flow rate of 1.4 m^3/hr. Orthorhombic (β) sulfur is amorphous in nature and most suitable for encasing other polymer materials to enhance coating longevity. Whereas monoclinic (α) sulfur is crystalline and subject to cracks and fissures which reduce coating life. Moreover, β sulfur readily converts to sulfur at about 60°C.

To retard the transformation from the amorphous to crystalline phase and thereby strengthen sulfur coating against cracking and deformation, Liu [67] produced a dicyclopentadiene-modified (DCPD-modified) sulfur coated urea in a fluidized bed. The DCPD-modified sulfur was obtained by simply mixing DCPD and sulfur at elevated temperatures for 1–6 hrs. To evaluate release characteristics, a certain amount of the coated urea was poured into a deionized water beaker kept at constant temperature and sealed with polyethylene film to avoid evaporation. A certain volume of water was periodically taken from beaker at regular intervals to analyze nitrogen concentration via spectrophotometry. The reduced water volume in the beaker was replaced with fresh water. The seven-day release rate of the sulfur-only coated urea was about 83% while the release rate for DCPD-modified sulfur coated urea was 53.5%, thus, giving a comparatively far better result.

Another technique was introduced by Detrick [68] for urea coating with sulfur as an inner coat to a secondary polymer coating. Here, the innovation permitted monomers to react on the surface of sulfur coated granules to form a polymer over-coating. The sulfur coating was then protected by the secondary polymer coat which proved more resistant to tackiness and mechanical degradations caused by impacts, abrasion, handling, transportation, storage etc. It presented good controlled release characteristics when compared to sulfur coated urea with an outer polymer coating. Urea granules were initially preheated in a fluidized bed and then spray coated with sulfur in a heated rotary drum. The resultant granules were then sprayed with diethylene glycol triethanolamine polyol and diisocyanate monomers in a second rotating drum with multiple nozzles. The seven-day dissolution rate was 38%. Detrick expanded this study to present another approach [69] that surpassed the previous in terms of enhanced controlled release attributes for sulfur coated urea. A triple layer coated urea was produced with an inner layer formed by on-surface polymerization of certain monomers (4,4-diphenylmethane diisocyanate, triethanolamine and diethylene glycol polyols). This was followed by a second layer of molten sulfur and a third outer layer produced by on surface polymerization of the aforementioned monomers. The controlled release period more than doubled that of the previous technique's result. Sulfur has been used to produce CRCU for decades. It also acts as a secondary plant nutrient and fungicide. It further possesses acidic properties that neutralize soil alkalinity. It is also a relatively cheap material that reduces the caking tendency of many fertilizers. When contrasted with many polymer materials used for urea coating, it is biodegradable [62, 64]. On the other hand, the crystalline nature of sulfur leads to the development of microscopic pores and cracks that induce significant brittleness [63, 69], and is also prone to higher friability when subjected to elevated temperatures in the soil. Due to its inherently augmented surface tension, sulfur coating appears to possess low wettability and adhesion to the urea substrate [64]. The sulfur-only coating is, therefore, not an effective sealant and requires additional conditioning materials that become vital for its application to urea granules which poses economic constraints. Since sulfur shells left in the soil are not immediately integrated, an excessive amount of sulfur may build up and react with water to acidify the soil [68].

The mechanism for the controlled release of sulfur coated urea comprises two steps: the burst effect and then continual release by diffusion as explained in chapter 1.

2.2 CRCU from polymer based coating materials

Polymeric materials were widely used to coat urea since sulfur coatings were easily disrupted by microorganisms whereas polymer coatings were not. The nutrient release from polymer coating is affected by diffusion as a function of coating thickness and soil temperature. However, polymer spray coating involves organic solvents that not only inflict additional costs of the lean solvent and solvent recovery, but also cause hazardous environmental emissions. Hence, the use of aqueous polymeric solutions was initiated to contain these shortcomings. Donida [70] studied urea coating using a commercially available aqueous polymeric material called Eudragit L30-D55® (methacrylic acid copolymers) in a two dimensional spouted bed with top spray orientation. The coating's composition is given in Table 1. Eudragit L30-D55® is mixed with water in addition to: talc, esthearates of magnesium, triethyl citrate, polyethylene glycol, and titanium dioxide to produce the CRCU. Higher atomizing air pressure and fluidizing air temperature produced a uniform coating film due to the production of smaller droplets and improved spreading of the suspension, respectively, resulting in a homogeneous layer. The coating thickness also imparted controlled release characteristics as it increased the thickness at a higher coating suspension rate and atomizing air pressure, but decreased with increased fluidizing air flow rate and temperature. However, elutriation was also caused at elevated air temperatures due to the premature drying of droplets before contacting the granules' surface.

The impermeable film on urea granules formulated by Eudragit L30-D55® was not effective for soils with a pH greater than 5.5. Also, low temperatures and high flow rates caused a rough coating surface. Therefore, it became imperative to optimize processing conditions using different coating compositions as mentioned in Table 1 [71]. In this case, nutrient release was measured by a static capture system in which filter paper soaked in H_2SO_4 was used to capture evolved nitrogen and an empirical process was used to measure its loss. The optimal fluidizing air temperature was 74°C, the optimal suspension flow rate was 11 ml/min and the optimal atomizing air pressure was 68.95 kPa, which produced a controlled release of evolved nitrogen at 3–57%. The authors extended this research by using vinasse as the solvent instead of water for the aqueous polymeric suspension [72]. Vinasse is an effluent of the ethyl alcohol industry that prevents pollution when used as an ingredient of the coating solution. Additionally, it also contains the plant nutrients nitrogen, potassium, calcium and magnesium. Therefore, Rosa [72] used vinasse instead of water to prepare a coating suspension from Eudragit with the same composition (Table 2.1) as previously reported [71]. The equipment, as well as the coating method and nitrogen volatilization measurements was also the same. The coating process was successfully carried out with the use of vinasse as a solvent and achieved a decrease in nitrogen volatilization up to 57%.

The permeability of water and urea in the coating film is a factor that governs release rate, release time and release pattern. Lan [73] studied the effects of various process parameters on the film's structure and permeability by coating urea granules in a Wurster type, fluidized bed apparatus. Polyacrylic acid latex with 40% solids was used as the coating solution. At elevated fluidizing air temperature and atomizing gas pressure, the coating film had a porous structure attributed to the poor spreading and pre-mature drying of droplets. Similarly, higher spraying rates resulted in reduced dewatering capacity by forming large pores on the coating's surface leading to poorly controlled release.

Wu [74] reported that thicker coating layers may damage soil quality if they are not degraded in parallel with nutrient release. With this in mind, urea coating with polyurethane is costly but its thinner coating layer was said to reduce coating cost by coating greater quantities of urea granules with less material. Coating was done in a rotating drum so that isocyanate, polyols and wax were added to urea granules for a certain period. The reaction between isocyanate and polyols formed a 10-15 μm thick polyurethane layer on the granules while paraffin acted as lubricant to facilitate the process. Water dissolution and soil incubation experiments revealed a 10% dissolution over the first ten days with 70-80% dissolution in thirty days followed by total release by forty fifty days. The release mechanism was the same as mentioned by Shaviv [35].

Table 2.1. Composition of coating suspension

Ref.	Weight % composition of coating suspension
70	Eudragit (16.7%), polyethylene glycol (0.75%), triethyl citrate (0.5%), esthearate of Mg (1%), titaniumdioxide (1.8%), pigment (0.2%), talc (2.75%),water (76.3%)
71	Eudragit (25%), polyethylene glycol (0.75%), triethyl citrate (0.5%), esthearate of Mg (3%), titanium dioxide (1.8%), pigment (0.2%), talc (3%), water (65.75%)
72	Eudragit (25%), polyethylene glycol (0.75%), triethyl citrate (0.5%), esthearate of Mg (3%), titanium dioxide (1.8%), pigment (0.2%), talc (3%), vinasse (65.75%)

Due to higher costs and process complexity along with issues of environmental pollution caused by polymers, research frontiers shifted towards developing low cost, easily fabricable and environmentally friendly materials [75]. Although the price of starch based coating was low, so was nutrient release longevity compared to polymer coating formulations, and furthermore, they were occasionally incompatible with crop metabolic needs [76]. Yang [76] employed waste polystyrene (thermocol) as a coating material mixed with wax and polyurethane as sealants for a more cost effective and controlled release urea fertilizer. Initially, polyurethane was prepared by dissolving and agitating diphenylmethane diisocyanate in ethyl acetate and castor oil, after which polyurethane was mixed with ethyl acetate-dissolved polystyrene. Urea granules were then spray coated with this solution in a Wurster fluidized bed followed by oven drying at 40°C for 24 hr to remove excess ethyl acetate. Nitrogen release was measured in still water at 25°C using the Kjeldahl method. The release rate slowed with greater coating thickness and the addition of wax to the coating solution did not have a significant effect. To the contrary, polyurethane effectively enhanced controlled release characteristics.

The development of controlled release and environmentally safe urea fertilizer was also studied by Mathews in 2010 [77]. Here, the conceptual advantage of the swelling capacity of certain polymers that retained strength enough to withstand osmotic pressure and avoid the burst effect during gelation, was explained. Urea was coated with a newly synthesized poly [N-isopropyl acrylamide]-co-polyurethane (PNIPAm-PU) and the controlled release of urea monitored by mass spectroscopy was observed as a function of the soil's temperature, pH and moisture. The coating solution was first synthesized with NMR characterization to validate the claimed structure. The Amino Terminated Poly N-Isopropyl Acrylamide (NH_2-PNIPAm) was synthesized by the radical polymerization of N-Isopropyl acrylamide (NIPAm) with potassium persulfate as the initiator and 2-aminoethanethiol hydrochloride as the chain transfer reagent in aqueous media. The next step involved the preparation of Isocyanate Terminated Polyurethane (NCO-PU-NCO) by degassing Poly (1,4-butylene adipate)diol end-capped (PBAG) at high temperature allowing this to react with 4, 40-methylene bis(phenyl isocyanate) (MDI) in a tri-necked flask equipped with a stirrer. In the third step, PNIPAm-PU was synthesized by the reaction of NH_2-PNIPAm with NCO-PU-NCO at 90°C. Urea granules were then dip coated in this solution, followed by centrifugal separation and vacuum drying. The proposed release pattern was similar to that mentioned by Yong [78]. In this study, the coating solution was set to vacuum drying; a time consuming, lengthy process.

To enhance nitrogen uptake efficiency of tea plants while studying controlled release behavior, Han [79] developed three different controlled release fertilizers. Urea granules were coated with Ca-Mg phosphate, polyolefin, and polyolefin plus dicyandiamide (DCD). The granules were placed in a concrete mixer with a smooth inner surface and the DCD, dissolved in dilute phosphoric acid, was sprayed onto the granules. The coated granules were then placed in a Ca-Mg phosphate powder and sprayed with wax sealant. Polyolefin and polyolefin plus DCD coated urea granules were also prepared in the same fashion. Pot and field experiments were done to study controlled release and nitrogen uptake by tea plants using all three coated urea samples. The polyolefin plus DCD coated granules produced the best results in terms of controlled release while maintaining optimal soil nitrogen concentration over the long term.

Petchsuk [80] reported the feasibility of poly (lactic acid-co-ethylene terephthalate) as a coating material. In a comparative study, urea granules were coated with commercial polylactic acid (PLA) and PLA, plus poly (lactic acid-co-ethylene terephthalate) which were synthesized by the authors. After dissolving this polymer in chloroform, it was sprayed on urea granules in a rotating mixing machine followed by two drying steps (hot air and heating gun). Controlled release properties were evaluated by monitoring the urea concentration by refractive indexing in a rotating bottle of water containing the coated urea granules. In addition, they also employed a scanning electron microscopic morphological study. The authors showed that controlled release was a function of the percent of coating applied, which, in turn, directly depended on the molecular weight, nature, concentration and frequency of the polymer coating. They also determined that controlled release was markedly affected by the coating's surface morphology.

1-Naphthylacetic-acid (NAA) has been reported to be a plant growth regulator (PGR) for the rooting of cuttings, fruit-set inhibition, fruit shedding and the initiation of flowering [81]. In 2012, Qiu [81] prepared CRCU with dual attributions of controlled release and PGR. To prepare the coating material, the monomers N-butyl methacrylate (BMA), methyl methacrylate (MMA) and 2-hydroxyethl acrylate (HEA) were added to a four-necked flask equipped with a stirrer, nitrogen supply and condenser. Benzoyl peroxide (BPO) (0.45%) dissolved in 5 ml of ethyl acetate was then added to the monomers and the mix was agitated under nitrogen with ethyl acetate for ~6 hr until a non-sticky material was produced. The non-reacted monomers were then precipitated by n-hexane and separated. The final poly (BMA-MMA-HEA) was air dried at 80°C. The solid coating material (PBMHs-NAA) thus obtained, along with the paraffin wax, was dissolved in ethyl acetate and the solution was then sprayed onto a fluidized bed of urea granules at 75°C for 25 min. The controlled release property of the coated fertilizer was determined by water dissolution followed by a urea concentration assay via UV spectrophotometry. The initial release rate was high (100% in eight days) due to the sticky adhesion of the granules which caused a rough surface. The addition of 10% paraffin wax, however, prolonged the dissolution: 1.54% at 24 hr, and 78.77% at 28 days.

Polymer coating materials have also been used to affect the controlled release of urea when urea acted as a constituent of compound fertilizers. For example, the combination, polyvinyl chloride/ polyacrylamide/ naturalrubber/ polylactic acid, was employed to coat a compound fertilizer containing urea, phosphorous, potassium, calcium, magnesium and copper [82]. Polyethylene and paraffin wax were used for the NPK compound fertilizer [83] and a polysulfone/cellulose acetate/polyacrylonitrile based coating by Tomaszewska [84-86]. However, the scope of our review does not cover coating materials for compound fertilizers as our focus is urea and those materials used as coating to enhance its controlled release.

Costa [87] studied the coating of urea granules with poly hydroxy butyrate (PHB) and ethyl cellulose (EC) using simple immersion and manual spraying with a pulverizer and triggler. PHB and EC were initially dissolved in chloroform and acetone, respectively, as the coating solution. Adjuncts were also employed to facilitate interface interactions between the coating solution and urea granules. The urea dissolution rate in distilled water was measured via indirect enzymatic conversion of urea to ammonia with a spectrophotometer to determine concentrations. The optimal coating material allowed complete urea release within 5 min, which was incompatible with set standards for agricultural use.

Polymer materials offer a number of advantages when used as coating materials for the controlled release of urea. They are biologically inert against microbial attack and provide a supply of nutrients consistent with crop metabolic needs over longer periods of time. They are also able to retain both micro and macronutrients within the helical polymer chain matrix [77]. Despite these advantages, polymer materials do have limitations. The coating processes are quite complex and involve a number of chemicals. The overall process does not attract commercial attention because of the high cost as most polymer materials require the use of organic solvents to formulate a coating solution. This not only increases costs due to solvents and their recovery, but also poses adverse environmental impacts in terms of hazardous emissions. Furthermore, many, if not all polymer coatings, are non-biodegradable after total nutrient release and present a new type of soil pollution that is undesirable. Hence, most controlled release urea fertilizers produced thus far have not been effectively admitted to commercial production. Even so, certain polymers have been employed to produce controlled release urea on a commercial scale; a glimpse of these is given in the next sections.

2.3 CRCU from superabsorbent/ water retention coating materials

Superabsorbent polymer materials (SPMs) have recently caught the attention of research circles because of interesting properties that favor CRCU production. These SPMs are 3-dimensional cross-linked hydrophilic polymers with an ability to imbibe water that is hundreds of times higher than their own weight and which cannot easily be removed even under extended pressure [88–95]. They find attractive use in agricultural and horticultural applications due to reduced water consumption and irrigation frequency, especially in drought prone areas and are thus considered economical. The advantages of SPM produced CRCUs include soil improvement through aeration, abatement of soil degradation, alleviation of water evaporation losses, reduction of environmental pollution through volatilization and leaching and a decrease in crop morbidity due to increased nutrition through enhanced nutrient retention periods [88-96].

Yong's study [78] opened new avenues of research for the production of multifunctional controlled release coated urea fertilizers with attributes of controlled release and improved water retention properties that are very beneficial, especially in regions with limited water supply. The most frequently used SPMs are classed as cross-linked polyacrylates/ polyacrylamides, hydrolyzed cellulose-polyacrylonitriles/ starch polyacrylonitriles graft copolymers and cross-linked copolymers of maleic anhydride. The general methods employed in most studies for SPMs as a coating material are based on either solution polymerization or inverse-suspension polymerization. The solution polymerization involves the blending of NH_3-neutralized acrylic acid (AA) or acrylamide (AM) based monomers in aqueous solution, followed by the addition of a water-soluble cross-linking N,N′-methylenebisacrylamide (MBA) and potassium/ammonium persulfate as initiators. The blending is continued at increased temperature until a rubbery product is obtained which is then dried, ground and sieved for coating purposes. For inverse suspension polymerization, the surfactant and dispersant are mixed to form a water-in-oil phase in which AA/AM monomers are blended with a cross-linker and initiator as described above. The resultant micro-spherical product is dried to form a free flowing powder that requires no grinding or sieving.

With this background, Guo [88] prepared slow release membrane encapsulated, double coated urea granules with an inner shell of crosslinked starch and an outer layer of acrylic acid and acrylamide. Soil incubation experiments determined nitrogen release by using the Kjeldahl method of distillation. Results indicated 10%, 15%, and 61% release rates on days two, five, and thirty, respectively. Coated urea, thus obtained, has cross-linked starch as inner coating layer with a copolymer of crosslinked acrylic acid and acrylamide as an outer coating. The slow release mechanism involves the absorption of water by the coating material which causes it to swell and transform to a hydrogel. The core urea then dissolves in the hydrogel's water and diffuses slowly through a grid like system of the swollen hydrogel via mass transfer of water from within the hydrogel to water in the soil. Another double coated urea with an inner coating of urea-formaldehyde and an outer layer of crosslinked poly (acrylic acid)/organo attapulgite composite was prepared by Liang [93]. He reported a dried CRCU released of 3.9%, 7.5% and 75% (wt.%) at two, five and thirty days of soil incubation, respectively. The release mechanism was similar to Guo's study with a slight difference: water, after diffusing through the outer coating, slowly penetrated the urea-formaldehyde layer to dissolve the urea which then escaped slowly by a dynamic exchange between hydrogel free water and soil moisture. The coating thickness and the solubility of urea-formaldehyde were characterized as controlling factors for the slow release. Hence, higher thickness and lower solubility produced the best slow-release outcome.

Liang [90] also prepared double coated urea granules with an inner layer of polystyrene and outer coating of cross-linked poly(acrylic acid)-containing urea. The urea release of the polystyrene coating was said to follow the same mechanism suggested by Shaviv [35] i.e. a three stage release mechanism: first came a lag period in which water penetrated the coating without urea release; then a constant release period followed when urea dissolved and flowed through the coating (burst effect) and finally, there came a stage of decline until the release of urea ultimately ended. The presence of the second coating layer in this study waived the burst effect in which more than 70% of the urea was released. Hence, the outer coating not only enhanced slow release but further facilitated effective irrigation due to water retention.

Some investigators have prepared controlled release urea fertilizers by either blending with superabsorbent materials or polymerization with a superabsorbent mixture. However, these slow release formulae have thus far experienced the undesirable “burst effect” that hampers the controlled release property. Some polymer shells also remain in the soil for a long time after nutrients have been completely released. Hence, an approach to enhance their biodegradability to avoid hazardous emissions and other effects was presented by Ni [94]. He prepared CRCU with an attapulgite matrix as the fertilizer core with two layers of coating: ethyl cellulose joined to a plasticizer as the inner coat, and a sodium carboxy methylcellulose (CMC) plus hydroxyethyl- cellulose (HEC) based hydrogel as the outer coat. Attapulgite is a type of octahedral Layered Mg-Al-silicate absorbent mineral with hydroxyl groups on its surface. It is almost inert towards salts (like urea), so it is preferred as a substrate for superabsorbent composite materials [95]. After 24 hr of soil incubation, the urea release rate was 8.7%. During this phase, water diffused gradually into the granules as slower release was facilitated by the hydrophobic ethylcellulose coating. During the second stage, from day two to five, there was consistent release caused by the diffusion of nutrients outwardly followed by dynamic mass transfer to the external atmosphere. In the last phase, from day two onwards, the solution's concentration within was lowered as bulk water was absorbed. During this stage, attapulgite absorbed the remaining nutrients which further enhanced the slow release of urea.

Another recent study by Yang et al. [97], addressed the issue of polymer biodegradability with double coated urea granules produced with biodegradable biopolyurethane derived from liquefied corn Stover as the inner coating, and a superabsorbent material based on chicken feather meal modified with acrylic acid as the outer coating. For the inner coating, urea granules were placed in a rotary drum and the coating solution was poured on rotating granules. Different runs were made to produce different mass coatings. For the outer layer, the acrylic-acid-modified-chicken-feather-meal (MCFM-AA) solution was poured on previously prepared coated granules followed by an adherent (MCFM-AA powder) to produce the final compact product. Release kinetics was studied in deionized water as well as in soil. The periodic increments in the mass coating of the inner coating layer caused significant reductions in release rates. For example, N release slowed from 1.5 days to 13 and then to 57 days as the mass of the inner coating increased from 3.2% to 5.3% and 8.5% (wt.%), respectively.

Tao [91] developed a triple polymer coated slow release urea with an inner coating of polyethylene, that primarily served as a slow release film, an intermediate coating layer of poly(acrylic acid-co-acrylamide) that served as a superabsorbent water retaining layer and an outermost coating of poly (butyl methacrylate) to protect the intermediate layer. The study intended to gain slow release while avoiding water evaporation losses with a goal to lessen irrigation frequency by the use of a multi functional superabsorbent slow release fertilizer. The three-layered coating operation utilized fluidized bed equipment that avoided nutrient loss due to high temperatures in the dip coating, which was easily amenable to up-scaling to pilot or industrial use. Slow release behavior was monitored by soil incubation. At a thickness of 25 μm, the release rate was 4.2%, 38%, and 56% respectively for days 1, 7 and 14 respectively. Similarly, at 50 μm it was 0.15%, 13.5%, and 24%; and at 75 μm it was 0.1%, 10.1%, and 10.3% on days 1, 7 and 14, respectively for both trials. The release mechanism was the same as described in Shaviv's work [35]. Hence, Tao demonstrated that nutrient release increased at elevated temperatures while the release rate was similar in both soil and water.

In 2012, Wang double coated urea in a pan granulator with k-Carrageenan-sodium alginate (kC-SA) as the inner shell and a cross linked k-Carrageenan graft, copolymerized with polyacrylic acid and celite (kC-g-poly AA/celite), as the outer shell [98]. Sodium alginate is an anionic natural macromolecule extracted from marine algae. Similarly, k-Carrageenan is an anionic polysaccharide extracted from red seaweed. The combination of both materials enhanced the mechanical strength of the coating layers and the hydrogel's brittleness which then eased water super-absorption. After coating, granules with a thin layer were dried and subjected to a duplicate coating step for better thickness. The same procedure was repeated to enclose kC-SA coated urea granules in a superabsorbent outer coating of (kC-g-poly AA/celite) followed by drying at 30°C to obtain the final product. Soil incubation experiments revealed 39%, 72% and 94% nitrogen release on days two, five and twenty-five, respectively. The release mechanism was the same as depicted by the same author in previous studies [88, 93].

The use of SPMs to produce CRCU offers a number of advantages, the most prominent being super-absorption of water combined with the controlled release of urea. However, the preparation steps are complex and required raw materials are costly. The CRCU products produced thus far offer higher costs which present a major impediment to their commercialization. Another aspect that prevents their commercialization is the non-biodegradability of some coating materials which causes a new type of soil pollution. However, this remains a relatively new research field and scientists are addressing these issues.

2.4 CRCU from bio-composite based coating materials

To obviate effects from the non-biodegradability of certain polymer coatings and to offset higher operational costs, the development of bio composite based coating materials for controlled release coated urea have recently caught interest in the research circles, with starch as a contender. Starch naturally occurs as a polysaccharide biopolymer that is abundantly available from many renewable plant sources. Due to its low cost, biodegradability, and abundance, several non-food applications of starch have been investigated, with starch based controlled release coating materials as one of the numerous areas. Since starch is hydrophilic, it cannot be used as a coating material on its own for CRCU preparations and requires blending with other materials for effective utilization [75, 99-103].

In 2005, Ito [104] prepared dual coated urea granules with an inner layer of poorly soluble isobutylidendiurea (IBDU) and the outer layer of starch with wax powder in a high shear granulator mixer using a simple blending technique. Through HPLC, he found that the nutrient release rate can be modified by adjusting both the fraction of dispersed, particles and the thickness of both inner and outer coatings. With only one coating (in the absence of an outer coating), that shell was subject to a diffusion release mechanism. The dual layer, on the other hand, followed a sigmoidal pattern of controlled release. The sigmoidal release pattern, as necessitated by some applications, refers to an initial slower release quantity followed by consistent increases. The proposed release mechanism followed a dual path. First off, the core nutrient shrunk in size after dissolution in water. Secondly, the concentration of the core nutrient solution kept decreasing until the concentration equilibrated within the reservoir. The release rate from a single layer preparation had soluble particles with a faster diffusion release pattern attributed to the formation of microchannels through which active nutrients immediately flowed. However, the dual layer product caused a sigmoidal release because of the hindrance offered by the outer, more impermeable layer.

Suherman [101] prepared a coating solution by mixing starch, acrylic acid and polyethylene glycol with slow additions of water and continuous stirring until a homogeneous mixture was obtained. The urea coating was carried out in a fluidized bed with a top spray of the starch based coating solution. Water dissolution experiments revealed reduced release rates with increased starch content of the coating. Higher temperatures enhanced the release rate because of the pre-mature drying of the coating droplets. Also, elevated temperatures reduced the proportion of liquid bridges on the urea granules, thus, leaving uncoated spots that permitted higher release rates later on.

In 2012, $K_2S_2O_8$ modified starch (ST) was prepared by gelatinizing starch with water at 80°C followed by cooling and mixing with $K_2S_2O_8$ at 60°C for 45 min [102]. The modified starch was graft polymerized with natural rubber (NR) latex by mixing and stirring at 60°C for 3hr in the presence of Teric®16A16 to produce NR-g-ST. The NR-graft polymerized starch was then used to encase urea granules to make CRCU. Coating was done by simple immersion of urea granules into the graft polymer blend followed by drying. The urea release rate in water, as determined by UV-vis spectrophotometer, was 21% in 24 hr. The diffusion mechanism of release was followed by nutrients so that only the core's shell remained; the core being hydrophobic natural rubber and a shell of starch. The hydrophilic nature of starch is associated with the presence of hydroxyl functional groups [99]. Various studies attempted to transform this hydrophilic nature to hydrophobic by the addition of different chemicals and additives. In most cases, consequent controlled release achievements did not correspond with crop metabolic needs, and thus, failed to meet standards (10-12 weeks) set by the scientific community.

Lignin is a cheap and natural macromolecular compound that is abundantly available as a waste material from pulp and paper industries [105]. Moreover, lignin is renewable, biodegradable, amorphous and a relatively hydrophobic bio-polymer compared to other polymers [106]. Perez [105] prepared a lignin based controlled release urea formulation by mixing urea and lignin in a glass reactor immersed in a thermostatic silicon oil bath. The mixture was heated and the resultant urea-lignin matrix was cooled to give a glass like structure that was later milled in a crusher to obtain the desired size range of controlled release particles. This study also included urea coating with ethyl cellulose in a Wurster fluidized bed. Ethyl cellulose predominantly possesses high physical and chemical stabilities with good film forming properties and is relatively less toxic. A 5% ethanol solution of ethyl cellulose was sprayed onto a fluidized bed of urea granules at 60°C followed by air drying in the same chamber at 70°C. Different runs were made to produce different coating thicknesses for the analysis. Both the lignin based controlled release urea particles and the ethyl cellulose coated granules were subjected to water leaching experiments to evaluate release rates. The patterns produced very slow releases in the early stage followed by a constant release leading to a period of decaying release. The coating's thickness, as reported by many others, had an inverse effect in terms of controlled release. The comparative study revealed that ethyl cellulose coated granules were better than the lignin based slow release urea formulation because of its coating uniformity which retarded water diffusion through the coating layer.

Mulder [106] employed soda flax lignin (Bioplast) coupled with acronal as a plasticizer and alkenyl succinic anhydride (ASA) as a hydrophobizing or cross-linking agent to produce CRCU. The urea granules were spray coated in a rotary pan coater with 25% bioplast dispersion as well as plasticizer and cross-linking agents at 70°C. Refractive index measurements were made to evaluate the amount of nitrogen released in water. Coating thickness and uniformity played key roles in the inhibition of urea dissolution. Coating uniformity is increased by spraying the coating suspension in three stages. In the first step, a sufficient quantity of suspension solids should engulf the urea granules in order to avoid the dissolution of urea during the process and which also allows the urea to become part of coating material. In the second and third steps, relatively small quantities of solids should be sprayed to fill fissures and micropores to contribute towards coating uniformity. Higher coating thickness granted better control release properties and the hydrophobizing action of ASA also played a key role in impeding urea dissolution. Furthermore, coating films with a plasticizer remained intact in water for two weeks and the cross-linker aided the coating layers and significantly reduced the release rate but still could not meet set market standards. It was, therefore, suggested to chemically modify cellulose to enhance control release properties.

Considering the swellability and biodegradability of konjac flour, Yong [78] prepared a controlled release urea fertilizer and studied its effect on various process parameters. A pellet of urea was initially heat molded to cake and then soaked in coating material. The coating consisted of compound polyether added to water, silicon oil and a catalyst that was fluffed uniformly under heat for 10 min. Heating and whisking continued with a further addition of toluene diisocyanate and konjac flour until the solution turned white. This was then spread on the caked urea. The coated urea was oven dried at 60-80°C, the setting temperature of the coating material. To study controlled release behavior, sodium hyposulfite titration experiments were used. Coated samples were buried in soil in beakers at constant temperature with an additional 500 ml of water. During the first 8 weeks, only a 20% release was observed which then rose to 70-80%. This is because the konjac flour initially absorbed water and swelled, which, in turn, inhibited urea release by narrowing exhaust channels. Later, the gelation of konjac flour occurred followed by microbial attack which disintegrated the material and assured rapid urea release. Soil burial tests at 70-90°C proved that the coating material was biodegradable. In another study, 5% acetone solution of ethyl cellulose and cellulose acetate phthalate at 30°C were used to coat urea beads in a Wurster fluidized bed unit at temperatures ranging from 32 to 51°C [107]. Soil incubation tests were done in a soil filled flask mounted on an orbital shaker kept rotating at 120 rpm. Released urea was analyzed by conductivity which indicated the release rate for coating with ethyl cellulose was higher than that of cellulose acetate phthalate. However, both coating materials were analogous in terms of the release mechanism. The three stage release rate was initially high, followed by a fairly constant release preceding a prolonged decline.

Vashishtha [108] showed that the dual advantage of sulfur coated urea i.e. controlled release of urea and availability of sulfur as a plant nutrient can better be achieved when phosphogypsum is used as the coating material instead of sulfur. This was likely because phosphogypsum is not only slightly soluble in water but also because it does not alter the soil pH (sulfur makes the soil pH acidic). Secondly, to transform sulfur coated urea to a plant available form (sulfate form), common sulfur must undergo bacterial transition whereas phosphogypsum, provides plant available sulfate readily. With this as a background, Vashishtha [108] employed both dry and wet methods to prepare phosphogypsum coated urea in a fluidized bed. The only difference between either methods was that the wet method (a mixture of phosphogypsum with neem oil, linear alkyl benzene, and water) was used to prepare the coating material; whereas, in the dry method, the same mixture was prepared without the addition of water. Neem oil and linear alkyl benzene were used as binder and surfactant, respectively. Water dissolution experiments were conducted with twice distilled water and with magnetic stirring until 100% dissolution took place. The dissolution rate decreased with increased coating thickness and the coating layer produced with the wet method was more effective than the dry preparation.

2.5 CRCU based on Neem Products

Shilpha et al. [109] conducted the incubation study to study the release pattern of nitrogen from neem oil, pongamia oil and castor oil coated urea in soil. The incubation study was conducted using light textured sandy loam soil by adopting complete randomized design. Neem oil coated urea recorded significantly higher availability of nitrogen (412.48 Kg ha^{-1} at 0-20 cm and 277.03 Kg ha^{-1} at 20-40 cm) at 45 and 60 DAI (Days after incubation) as compared to other oil coated urea due to slow solubility and slow release of nitrogen.

Gnanavelrajah et al. [60] explaining the use of nitrification inhibitors as one of the measure of reducing nitrate leaching showed that neem (Azadirachta indica A. juss) cake and its extract have nitrification inhibitory properties. Leaching experiments were conducted using undisturbed soil columns under laboratory conditions to investigate whether blending neem cake with nitrogen fertilizer reduces leaching losses in reddish brown latosolic (rhodudults) soils of Sri Lanka. The treatments used were urea/ammonium sulphate at the rate of 250 kg N/ha, urea/ammonium sulphate + 20% neem cake (w/w) and urea/ammonium sulphate + 30% neem cake (w/w). Greenhouse pot experiments were also conducted with radish (Raphanus sativus) to examine whether neem materials when blended with N fertilizer influence the response to nitrogen fertilizer. Neem cake treatments, at both 20% and 30% levels, significantly reduced leaching losses of nitrate with both urea and ammonium sulphate. Application of neem cake and extract with N fertilizer gave significantly higher yield of radish compared to the fertilizer alone treatments. Thus it was pointed that using neem materials increase the agronomic efficiency of N fertilizer and also reduce pollution caused by nitrate leaching.

Kumar et al. [110] showed that the nitrogen (N) fertilizer-use efficiency (20-50%) is low in rice fields in India. However using neem-oil coated urea can increase N-use efficiency in lowland rice, but the desirable thickness of neem-oil coating onto urea is not known yet. Therefore, field experiments were conducted during kharif (rainy) season of years 2004 and 2005 at the Research Farm of Indian Agricultural Research Institute, New Delhi to know the suitable thickness of neem-oil coating on prilled urea (PU) for increased N-use efficiency and yield. The treatments comprised of twelve combinations of four N sources (PU coated with neem-oil thickness of 0, 500, 1000 and 2000 mg kg^{-1} PU) and three N levels (50, 100, and 150 kg N ha^{-1}) plus a no-N control. Prilled urea (PU) refers to the common urea available commercially in prills, which is different from urea super granules. Application of urea coated with neem-oil thickness of 1000 mg kg^{-1} PU resulted in significantly higher growth, yield parameters, grain yield, N uptake, and efficiency of aromatic rice (Oryza sativa) over uncoated PU. Nitrogen application at 122 kg ha^{-1} was optimum for increased yield of rice. Nitrogen-use efficiency decreased significantly and substantially with each successive increase in levels of N from 50 to 150 kg ha^{-1}.

Kumar et al. [111] in their another work highlighted the utility of neem (Azadirachta indica A Juss) oil coated urea as a value-added nitrogenous fertilizer. In the study, the expeller grade (EG) and hexane-extracted (HE) neem oils, the two most common commercial grades, were used to prepare neem oil coated urea (NCU) of various oil doses, for which mineralization rates were assessed in four soils at three incubation temperatures (20, 27, and 35°C). Neem oil dose-dependent conservation of ammonium N was observed in NCU treatments in all of the soils. However, a longer incubation period and a higher soil temperature caused depletion of ammonium N. Overall, the nitrification in NCU treatment averaged 56.6% against 77.3% for prilled urea in four soils. NCU prepared from EG neem oil was consistently superior to that derived from hexane extracted oil. The performance of NCUs was best in coarse-textured soil and poorest in sodic soil. The nitrification rate (NR) of the NCU in the soils followed the order sodic > fine-textured > mediumtextured > coarse-textured.

2.6 Commercially available controlled release coated urea (CRCU)

Despite high operational costs, CRCUs have been produced and sold on commercial scale. However, most of these products have been limited to horticultural and ornamental applications rather than large scale agriculture. The Tennessee Valley Authority (TVA) pioneered the commercialization of CRCU with a large scale production of sulfur coated urea. The Arthur Daniels Co. (ADM) was the first to produce polymer coated fertilizers using dicyclopentadiene with glycol ester. Table 2.2 provides an overview of coating materials that have been used to produce CRCU on a commercial scale thus far.

Table 2.2. Coating materials used to produce CRCU on commercial scale

Commercial name	Composition of coating material	Company/provider	Ref.
SCU	Sulfur + wax + diatomaceous earth + coal tar	Tennessee Valley Authority (TVA) USA	[112]
Meister	Polyolefin + inorganic powder	Chisso Co. Kitakysya Japan	[112–118]
LP30 ~ 180, LPS40 ~ 200 LPSS 100	Polyolefin	Chisso-Asahi Fertilizer Corporation	[119–122]
CRU	Polymeric material	Agrium Inc. Calgary	[123]
CU & CUS	Polymeric material	Chisso-Asahi Fertilizer Corporation	[124]
PCF	Polyurethane-like	Haifa Chemicals Co. Ltd.	[125,126]
Zn-coated urea	Zinc oxide	Indo-Gulf Fertilizers, Jagdishpur (UP), India	[127]
Agrium PCU	Polymeric material	Agrium US Inc.	[128–131]
Kingenta PCU	Polymeric material	Shandong Kingenta Ecological Engineering Co. Ltd. China	[128, 132,133]
Humate coated urea	Humic acid	------	[112]
PCU	Polyolefin		[134]

2.7 Concluding remark based on Literature review

The coating of urea is required to avoid nitrogen loss through leaching, volatilization, and denitrification. CRCUs inhibit this loss and serve to release nitrogen in a mode that is compatible with the metabolic requirements of plants. Millions of dollars have been spent to develop numerous coating materials and techniques; even so, the production of CRCU has not yet reached to a wider industrial scale. Sulfur alone cannot be effectively used as a coating material to produce CRCU because of its amorphous nature. Many sealants, binders, plasticizers and protective agents have therefore been used to combat the immediate burst effect, all of which increase process complexity and costs, which is why the production of sulfur coated urea has almost been abandoned. CRCUs based on polymer/superabsorbent materials offer promising potential in terms of extended controlled release and water retention, but the complexity of processing, elevated costs and the non-environmentally friendly side effects of some materials prevent industrial scale production. A relatively small research quantum is reported with regard to the production of CRCUs with starch, lignin and cellulose based coating materials, which are relatively cheaper, biodegradable and renewable. However, their augmented hydrophilicity and limited controlled release characteristics are weak points.

However NCU which is now produced in India holds substantial promise to become a effective CRCU particular in tropical counties where the Neem tree is present and availability of Neem oil is not a limiting factor.

Some of the suggestions emanating out of above extensive review are:

1. The production of CRCU should begin with original industrial grade urea granules rather than melting, transforming, dissolving or polymerization to fabricate controlled release matrices with other materials.
2. Coating material should be selected with a view to its (i) affinity with urea; (ii) its ability to permeate water and urea solution; (iii) its capability to impede immediate urea escape from the coating surface; and (iv) its ability to release urea in a manner that meets a crop's metabolic requirements over a specified period of time. It should also be biodegradable and cheaper. Apparently, no such material(s) exist which possess these ideal traits. However, bio composites based on starch/lignin/cellulose can indeed be modified to significantly achieve such properties.
3. The coating process should enable industrial production of CRCU without changing the spherical geometry of urea granules. For this reason, a fluidized bed coater, pan coater or rotary drum coater may be employed. Due to its excellent heat and mass transfer characteristics in addition to its easy operation, fluidized bed coating is a good candidate for industrial scale production. However, when using the fluidized bed, coating materials should be compatible with effortless spraying of the fluidized bed of urea granules.
4. The granulation process can be used to produce controlled release urea granulates. Analytical grade urea can be either blended or made to physically react with a suitable material (with the same aforementioned attributes) that best constructs a controlled release formulation which can then be converted to appropriate granular sizes and shapes as needed. For this purpose also, the fluidized bed granulator can successfully be employed.

CHAPTER 3

Preparation, Characterization and Experimental Determination of Nutrient Release from NCU

With an increasing awareness towards human health and environmental protection, there is a rapid shift towards development of eco-friendly fertilizer based on natural resources. The development of CRF based on natural product coatings is thus a green technology that not only reduces nitrogen loss caused by volatilization, leaching and gaseous emissions but also alters the kinetics of nitrogen/nutrient release, which, in turn, provides nutrients to plants at a pace that is more compatible with their metabolic needs. NCU is one such CRF prepared using natural product.

In the present chapter various aspects *viz.* preparation, characterization and experimental determination of nutrient release from NCU are discussed. Section 3.1 covers preparation of NCU using fluidized bed setup. Section 3.2 presents physical and chemical analysis of uncoated urea (UCU) and NCU using various analytical methods/techniques. Section 3.3 discusses experimental determination of nutrient release from NCU in water domain. Section 3.4 presents a rapid technique for determination of nutrient release from NCU in water domain. Section 3.5 discusses experimental determination of nutrient release from NCU in soil domain.

3.1 Preparation of NCU

Commercial UCU granules with a nitrogen content of 46.44% (label specification) and distribution of particle diameter from 0.5 mm to 2.8 mm (determined using sieve analysis) were supplied from Chambal fertilizer & Chemical limited (CFCL) Gadepan, Kota (India). The urea particles were coated with Neem oil supplied by Shubhra industries, Jaipur (India). The properties of urea and Neem oil used are given in table 3.1.

Table 3.1 Properties of Neem oil and Urea

Neem oil		**Urea**	
Iodine Index	81.28	Chemical Formula	$(NH_2)_2CO$
Kinematic Viscosity [30°C] (m^2/s)	43.75	Molecular weight	60.06
Saponification value	199.86	Odor	Odorless
Physical state at room temperature	Liquid (golden yellow)	Absolute Viscosity [20°C] (kg/m-s)	0.185
Acid value	32.538	Density (kg/m^3)	1320
Cloud point (°C)	13	Melting point (°C)	133-135
Pour point (°C)	7.0	Flowing time (20°C) (Second)	25-40
Density at room temperature (kg/m^3)	918.2	Solubility in water (kg/m^3)	1079 at 20°C 1670 at 40°C

Various methods are available for making coated urea which acts as CRF [45]. Among the available techniques as explained in concluding portion of chapter 2, fluidized bed coating process, being one of the oldest and experimentally simple to design and operate for forming small coated particles also holds promise for making NCU of reasonable quality. The experimental set up used and line diagram is shown in figure 3.1(a). The NCU obtained after coating is shown in figure 3.1 (b)

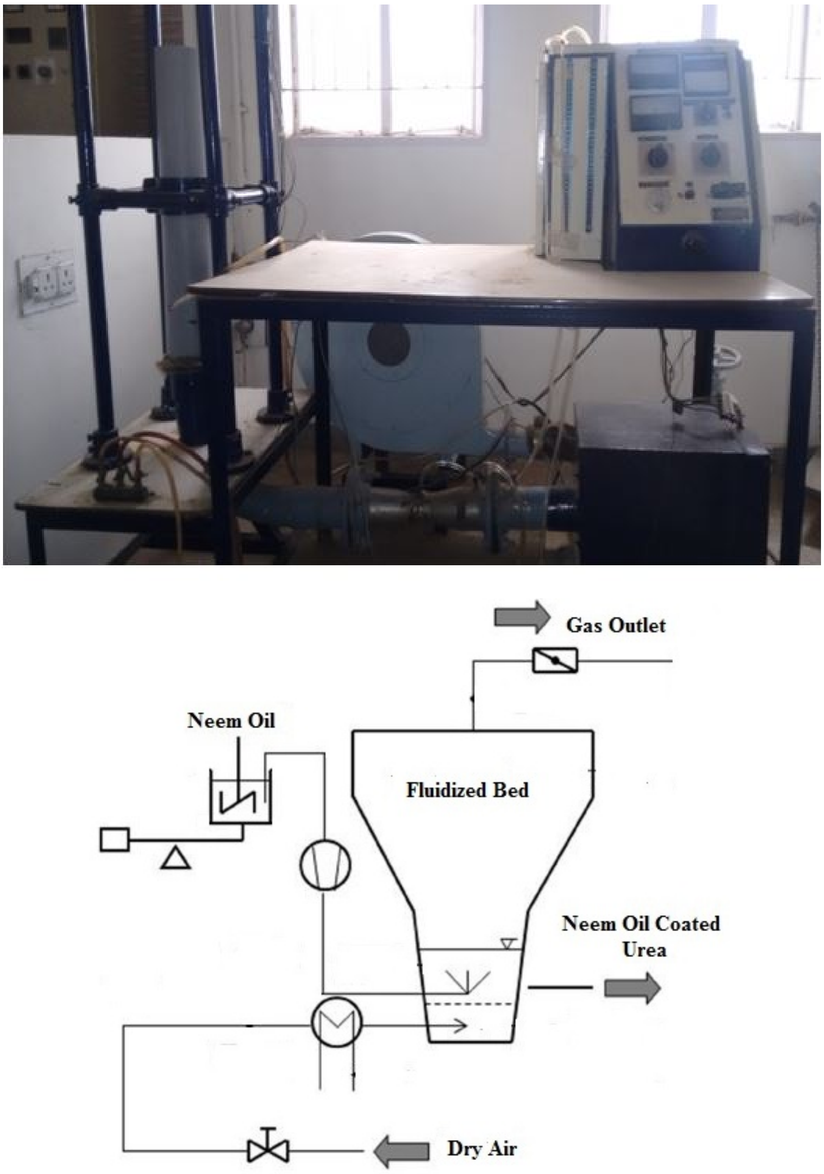


Figure 3.1. (a) Fluidized bed coater: Experimental set up and its line diagram

Figure 3.1. (b) NCU obtained from UCU after coating in Fluidized bed coater

The fluidized bed was made from a flexi glass. A spraying nozzle of an air-atomized nozzle was centrally set above the fluidized bed. A batch of UCU 210 g in weight were put in the fluidized bed and the bed was fluidized at higher than their minimum fluidization. For coating 20 ml of Neem oil at room temperature and flow rate of 0.35 ml/min, under a pressure was atomized with compressed air, and sprayed onto the urea particles in the fluidized bed for coating. Steady state was indicated by a constant bed temperature and constant head. Final product samples were collected after 20-30 min of fluidization. By this time urea particles were uniformly coated with the neem oil.

3.2 Physical and chemical analysis

3.2.1 Particle size analysis

Particle size of fertilizer products and/or fertilizer raw materials is defined as the particle diameter ranges of the test material. Particle size affects agronomic response, granulation techniques, storage, handling, and blending properties. The particle size distribution was determined for both UCU and NCU using standard sieve analysis (dry sieving as per IFDC S-107) [136]. For this analysis a sample weight of 210 g was used for both UCU & NCU and the resultant distribution is as shown in figure 3.2. It can be seen from the figure that maximum particles are available in diameter range of 1.7 mm and 2.0 mm. Also it can be inferred from these results that particle strength also increases due to coating (reduction in particle breakage after neem oil coating) since less number of particles of NCU are present in lower size distribution ranges.

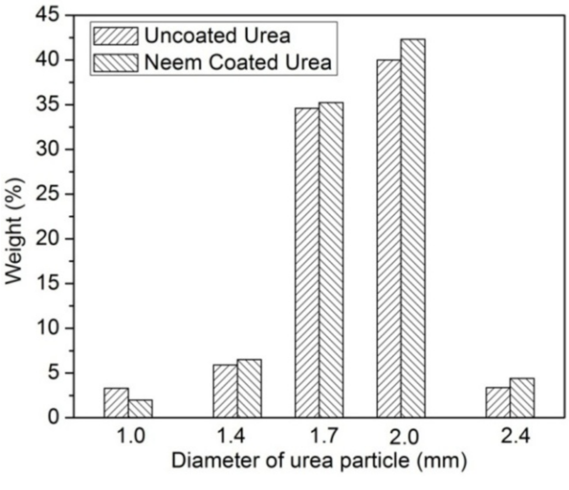


Figure 3.2. UCU and NCU particle size distribution

3.2.2 Percent coating

The actual coating percent is determined by taking a 10 g NCU sample, immersed in 100 ml of distilled water. After thorough shaking the urea gets dissolved in the water and as a result the coating was liberated from NCU. Subsequent filtration and water evaporation gives the coating % which is calculated using equation 3.1.

$$\text{Coating } \% = \frac{[M_i - M_o]}{M} \mathbf{x}\, 100 \tag{3.1}$$

Here,

M_i : weight of filter paper with urea sample, after evaporation (g),

M_0 : weight of filter paper (g),

M : weight of urea sample (g)

$$\% \text{ Coating } = \frac{[0.57]}{[10]} \text{x } 100 = 5.7\%$$

3.2.3 Nitrogen content

The nitrogen content of NCU is estimated using the standard Kjeldahl method [61]. The sample was treated with sulphuric acid to yield ammonium sulfate. The hydrolysis of ammonium sulfate yields the nitrogen content. Also the nitrogen content can be calculated mathematically using the total coating percentage as given in the equation 3.2.

$$\text{N } \% = 46.44 \, \frac{[100 - \text{Coating } \%]}{100} \tag{3.2}$$

Nitrogen content values of UCU and NCU obtained experimentally and using equation 3.2 are almost same, which are shown in table 3.2. The value obtained by equation 3.2 is used in present work.

Table 3.2. Nitrogen Content in UCU and NCU

Sample	**Coating, %**	**Urea, %**	**% N (experimentally)**	**% N (equation 3.2)**	**Nitrogen, % (used in present work)**
UCU	0.00	100	46.34	46.44	46.44
NCU	5.7	94.3	43.69	43.79	43.79

3.2.4 Dustiness factor

Dustiness is a physical property of fertilizer. Due to the large quantities of fertilizers produced and raw materials handled in bulk, their dustiness is of particular concern and can cause various problems like, a significant quantities of material can be lost during processing, handling and application resulting in monetary losses to the manufacturers and users. Also, environmental pollution and exposure of employees to hazardous levels of dust is not indicative of a responsible organization. So dustiness of fertilizer is an undesirable property. The dustiness was measured by taking 10 g of NCU in a bunker funnel, in which compressed air is passed from the bottom with 10 Psi of pressure. After 5 min sample is removed from the bunker funnel and then weighed. The weight loss is calculated. The amount of weight loss is called dust. In our case loss in mass of the sample = 0.037 g, so % Dustiness = 0.037/10*100 = 0.37% which is in agreement with the values reported in literature for other CRF [108].

3.2.5 Dissolution rate

The UCU obtained from market and NCU samples prepared as discussed above were analyzed for dissolution rate. To obtain the dissolution rate 5 g of sample particles (of same diameter of 1.7 mm) were put in a beaker containing 50 ml of double distilled water. For mixing magnetic stirrer was used at constant speed. The time required for complete dissolution of urea was noted down. Temperature was also varied to see its effect on dissolution and as expected dissolution rate was slower for NCU as compared to UCU and dissolution rate (indicated by lower dissolution time) increases with temperature as can be seen from results given in table 3.3.

Table 3.3. Dissolution rate of UCU and NCU

Sample (diameter = 1.7 mm)	**Dissolution Time (sec)**				
	30°C	**35°C**	**40°C**	**45°C**	**50°C**
UCU	324	300	287	239	210
NCU	482	445	426	372	357

3.2.6 Crushing strength

The crushing strength is an important parameter which indicates the ability of a particle/material to withstand the physical handling throughout the supply chain. Experimentally it is measured by applying a pressure to individual granules, usually of a specified size and noting the pressure required to fracture each granule. In present work, the test was performed on the different size (1.7 mm & 2.0 mm) particles of NCU and UCU. A tensile strength tester (Make Shimadzu available at Material Research Center of Malaviya National Institute of Technology, Jaipur) as shown in figure 3.3, was used for measuring crushing strength in which granules were subjected to a force applied by a metal plunger that was a part of the apparatus and the values were noted down.

Figure 3.3. Tensile strength tester used for UCU and NCU particle

The results of crushing strength of NCU and UCU for two different diameters namely 1.7 mm and 2.0 mm are shown in table 3.4.

Table 3.4. Crushing strength of NCU and UCU

Sample	**Crushing strength (N/mm^2)**	
	(dia=1.7 mm)	**(dia=2.0 mm)**
UCU	1.49	1.62
NCU	2.50	2.96

From the above values it can be inferred that NCU particles have higher crushing strength as compared to UCU of same size indicating its higher mechanical strength which is helpful in storage and transportation. Higher crushing strength leads to a reduction in attrition during storage and transportation and also reduces the dustiness factor. The crushing strength increases with the increase in size of particle for same sample.

In order to compare the crushing strength of NCU with other CRF, polymer coated urea (PCU) and bentonite coated (BCU) with chitosan as a binder were selected. PCU and BCU crushing strength from literature values [137] were taken. These particular CRF particle were selected because the literature values of crushing strength of these CRF were available for particle with same urea core radius and coating thickness as the NCU prepared The results are shown in table 3.5. From the table it is clear that NCU has higher crushing strength as compared to PCU and BCU indicating its better performance as CRF due to improved strength.

Table 3.5. Comparison of Crushing strength of NCU, UCU, PCU and BCU

Sample	**Crushing strength (N/mm^2)** **(dia=2.0 mm)**
UCU	1.62
NCU	2.96
PCU	1.80
BCU	1.67

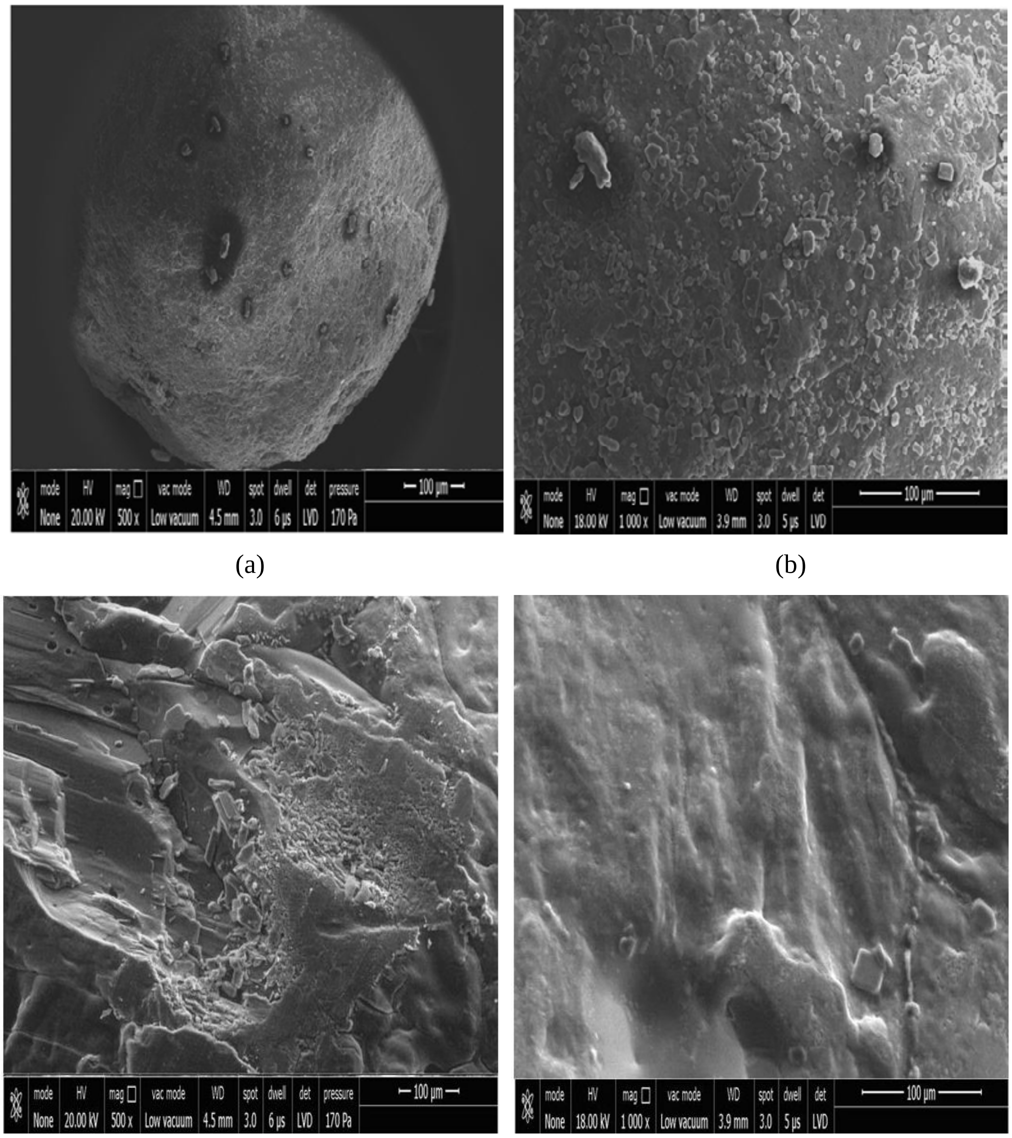
3.2.7 Morphology and microscopic analysis (SEM) of the surface

Scanning Electron Microscopy (SEM) with an energy dispersive analysis system of X-ray spectrometer (EDX) is one of the powerful analytical tool to study the morphology and relative elemental composition of the granules. Thus, morphology and relative elemental concentration of UCU and NCU were determined using scanning electron microscopy (SEM) (Make: Nova Nanosem-450 FEI, available at Material Research Center of Malaviya National Institute of Technology, Jaipur) as shown in figure 3.4 which was equipped with an energy dispersive analysis system of X-ray spectrometer, EDX. For analysis UCU and NCU samples were dispersed over a carbon tape pasted on the surface of a metallic disk (stub). Then, the disk was coated with gold in an ionization chamber and then the samples are ready to be analyzed.

Figure 3.4. *SEM with EDX used for UCU and NCU particle*

Samples were observed using SEM to find layering and agglomeration. Layering is a desirable trait for the particle coating. An irregularity in coating thickness and shape of granules was observed. UCU and NCU particles of 1.7 mm diameter were selected randomly and observed under SEM at magnifications of 500X and 1000X. SEM images are shown in figure 3.5 (a and b) for UCU and figure 3.5 (c and d) for NCU.

In case of UCU long crystals were tightly cemented with the finer ones on the surface of the urea (figure 3.5 (a-b)). This morphology can be attributed to the fact that production of uncoated granular urea production involves agglomeration. Some pores and gaps are also visible. However, for NCU (figure 3.5 (c-d)) coating imparts more homogeneity to the surface and since neem oil coating is dense, no visible sign of gaps or cavities in coating layer were observed.

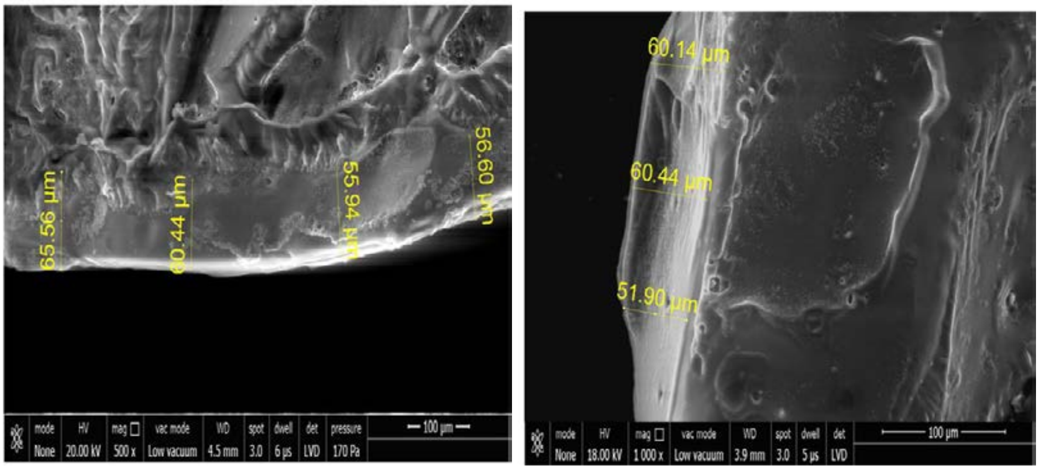


(a) (b)

(c) (d)

Figure 3.5. SEM image of UCU [a (500X) and b(1000X)] and NCU [c(500X) and d(1000X)] granules

To get an estimate of coating thickness, NCU particles were cut with a sharp knife and these broken particles were scanned using SEM as shown in figure 3.6 (a-b). A variable coating thickness lying between 51.91 µm to 65.56 µm was observed. As can be seen in the images the coating layer is very dense, the contact between the coating layer and the urea granule was thorough. This dense coating is responsible for imparting controlled release behaviour in urea. It is reported that the thickness of coating fertilizers affects the release pattern of nitrogen from fertilizers [135].



(a) (b)

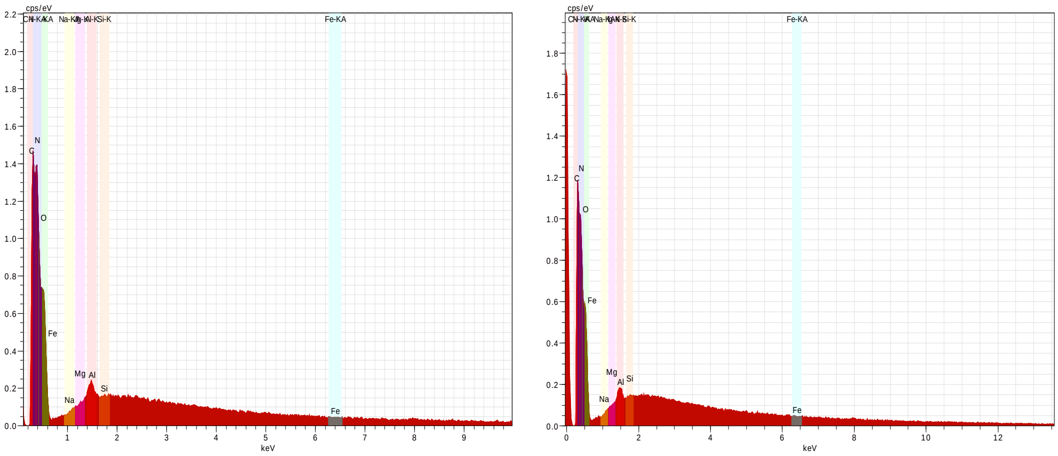
Figure 3.6. SEM [a (500X) and b (1000X)] image of a section of NCU granules

EDX of UCU and NCU

X-rays generation in a SEM occurs in a two-step process. In first step, the electron beam hits the sample and thereby transferring a part of its energy to the sample atoms. Energy so absorbed by sample atom manifest itself either in form of the electrons of the atoms jumping to a higher energy shell or may be completely knocked-off from the atom. In the latter case the electron leaves behind a hole which is positively charged. The second step comprise of transition of the negatively-charged electrons from higher-energy shells to fill the hole of the lower-energy shell, the energy difference between this transitions is released in the form of an X-ray.

The X-ray so generated has an energy which is characteristic of the energy difference between the two shells. It thus depends on the atomic number, which is a signature of every element. In this way, X-rays form the unique fingerprint of every element whereby helping in identification of the element type present in a sample. EDX generate the date in form of spectra in which the peaks corresponding to different elements present in the sample are formed.

The EDX of UCU (figure 3.7 a) and NCU (figure 3.7 b) showed no remarkable difference in presence of any extra elements in NCU as compared to UCU. However lower peak of nitrogen in case of NCU suggests that about 2% reduction in total N was observed for NCU as compared to UCU. It is due to inherent nature of the coating process, in which the urea granule undergoes, spraying, wetting and drying process which may cause some loss of nitrogen [137].



(a) (b)

Figure 3.7. EDX Diagram of (a) UCU and (b) NCU

3.2.8 Fourier transforms infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy is a powerful tool to study the chemical species and functional groups present in a sample. FTIR spectroscopy (Make: Perkin Elmer company available at Material Research Center of Malaviya National Institute of Technology, Jaipur) as shown in figure 3.8 was used to analyze the fertilizer samples.

Figure 3.8. FTIR used for UCU and NCU particle

The UCU and NCU granules were dispersed in dry KBr powder and then ground to obtain fine particles. These particles were analyzed at wavelength range from 4500 cm^{-1} to 400 cm^{-1}. All spectra were recorded at ambient temperature.

FTIR spectra analysis for UCU and NCU

The FTIR spectra (figure 3.9) of UCU and NCU show no significant variation in peaks observed indicating that there is no chemical interaction between the urea and the coating material. Both the samples show similar strong peaks of amide group, N─H at 3500 cm^{-1}, indicating the presence of urea molecule. This is followed by the double peaks of C═O bonds at around 1682 cm^{-1} and C-N bond around 1465 cm^{-1}.

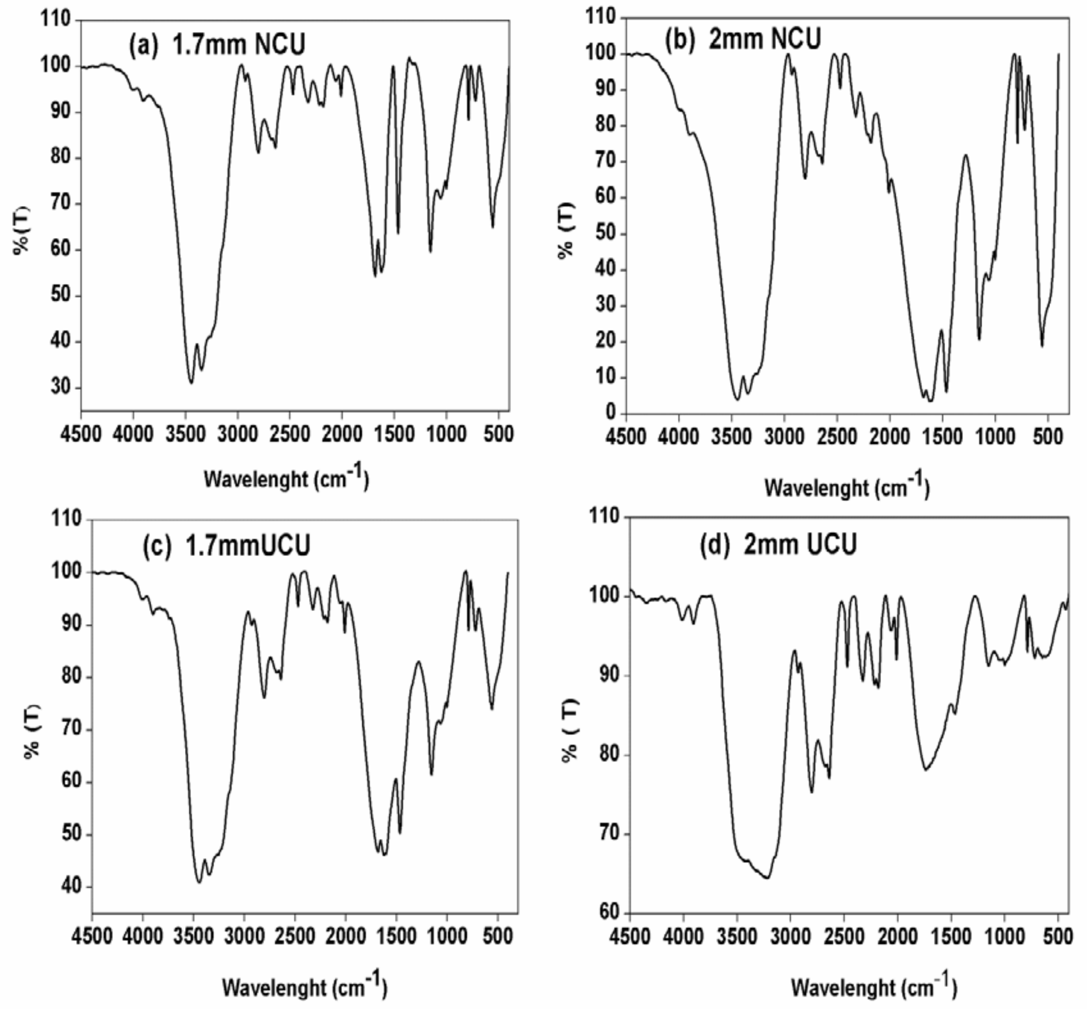


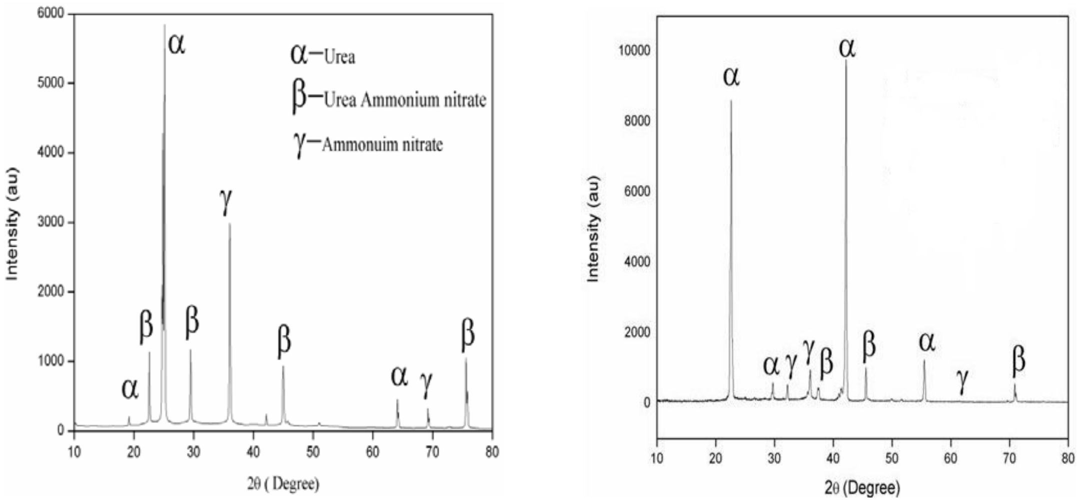
Figure 3.9. FTIR Diagram of NCU and UCU

3.2.9 X-ray diffraction (XRD) analysis

It is a rapid analytical technique primarily used for phase identification of crystalline materials and can provide information on unit cell dimensions. The analyzed materials are finely ground, homogenized and average bulk composition is determined by XRD machine (Make: ‘X' Pert powder PANalytical, available in Material Research Center in Malaviya National Institute of Technology Jaipur) as shown in figure 3.10. It works on Bragg’s law ($2d \sin \theta = n\lambda$). The XRD patterns were recorded in the range of 2θ equal to 20^o-80^o. It was used to explain the interference pattern of X-rays scattered by crystal.

Figure 3.10. *XRD used for UCU and NCU particle*

The XRD spectra of the UCU and NCU of particle diameter 1.7 mm are compared in figure 3.11. From the figure it is evident that there are only minor differences in the position and intensity of the peaks between the spectra of prepared materials (NCU) and the starting fertilizer (UCU). This is attributed to the strong physical adherence of Neem oil with the outer coating of urea base. All the recorded peaks correspond to the components of the fertilizer. Since no new peaks in the spectra of NCU are observed, it may be inferred that no new phases are formed during the coating process. It may be concluded that the interactions between the Neem oil and Urea are basically physical and not chemical in nature.



(a) (b)

Figure 3.11. XRD diagram of (a) UCU and (b) NCU

3.3 Experimental determination of nutrient release from NCU in water domain

An accurate estimate of nutrient release pattern from CRF is required both for manufacturers as well for farmers since it helps them in understanding fertilizer potency and nutrient planning for the crops. Although the field tests provide a better estimation of the nutrient release behavior, however, it suffers from inherent constraints of being influenced by the variation in environmental conditions like temperature, soil moisture, soil pH, soil microbes population and porosity, etc. Thus, determination of nutrient release under laboratory conditions provides a convenient, useful and nearly accurate approach to understand nutrient release mechanism. Other researchers have also pointed that laboratory experiments were successfully in predicting nutrient release rate of CRF [138-140]. In actual practice the estimation of nutrient release in soil is more pertinent since it depicts the actual behavior under field conditions however as explained in chapter 1 the mechanism of nutrient behavior in CRF is mainly governed by water penetration into the core through coating. Thus, the study of nutrient behavior in water domain gives a fairly accurate picture of nutrient release and this is experimentally done first followed by studies in soil domain to improve the predictions. In present work the nutrient release in water from NCU is experimentally determined using UV-Vis spectrophotometer and refractometer.

3.3.1 Experimental study of nutrient release from NCU using UV-Vis spectrophotometer

UV-Vis spectrophotometer provides a simple experimental approach to understand the nutrient release from NCU. The samples of NCU are first used to prepare standards for calibration curve. Five NCU solutions were prepared with concentrations: 0, 100, 500, 1000, 2000, 5000, 10000 ppm. UV-Vis double beam (Make Shimadzu, model UV-1800 available in the research lab of the Chemical Engineering department at MNIT Jaipur) as shown in figure 3.12 is employed to measure the optical density of the above standards at a wavelength of 210 nm.

Figure 3.12. UV-1800 Spectrophotometer Double Beam used in experiments

Nutrient release test

For conducting the release test 2±0.001 gm of NCU particles (diameter 1.7 mm) is immersed into 250 ml of distilled water and placed at room temperature. This particular amount of NCU is taken to ensure that urea concentration remains in the range of the calibration curve during the course of conducting the release test. After every 2-4 days, NCU concentration is determined by UV absorbance at 210 nm. Distilled water is added to the fixed point (250 ml) before and after the sampling process. The released nutrient is then calculated from the NCU concentration and the experiment ends as the released nutrient reaches 98.27%. Two repetitions were performed in the release test for the sake of attaining accuracy in the results. The flow chart for the experimental determination of nutrient release is shown in figure 3.13.

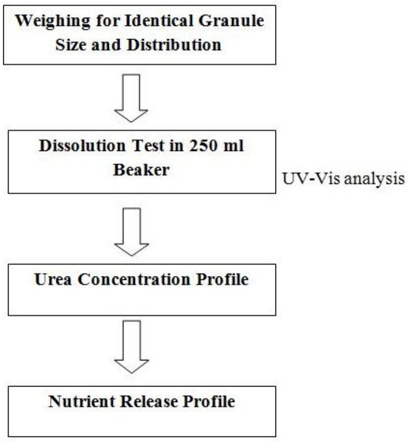


Figure 3.13. Flow chart for experimental determination of nutrient release

NCU calibration curve

Figure 3.14 shows a NCU calibration curve in distilled water constructed with standards from 10 to 10000 ppm. The calibration curve so obtained is empirically given by the equation: y =0.178x with R^2=0.9949 where x and y present NCU concentration in ppm and its absorption in mili absorption unit (mAU) respectively. The curve depicts linearity over a wide range, which helps in the measurement of nutrient release from NCU without dilution of samples.

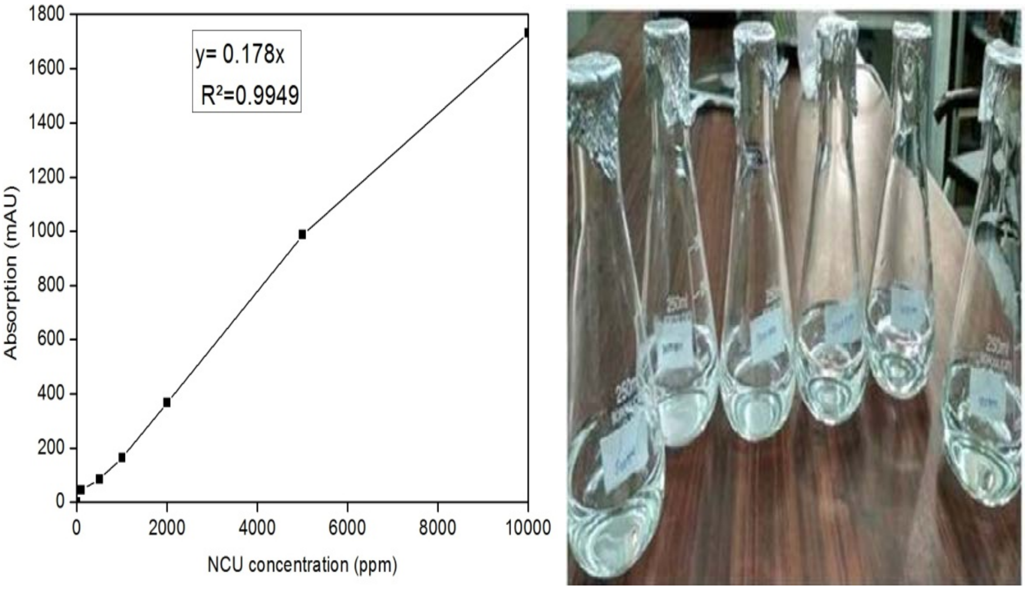


Figure 3.14. Calibration curve for NCU at 210 nm and NCU samples

Nutrient release behaviour

The release profile determined experimentally from NCU is shown in figure 3.15. The release profile shows a sigmoidal shape and follows the diffusion stages as described in literature [141, 142]. From the profile so obtained it is clear that in first eleven days, the percent nitrogen/nutrient release is 6.35%. This increases to 16.82% at the end of 19 days. Thus, up to 19 days the *lag period or stage* is observed, which is attributed to the fact that, mainly water vapor penetrates into the NCU granule and dissolves a small fraction of solid fertilizer. The driving force responsible for this process is the vapor pressure gradient across the Neem coating. The volume available to the condensed vapor 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.

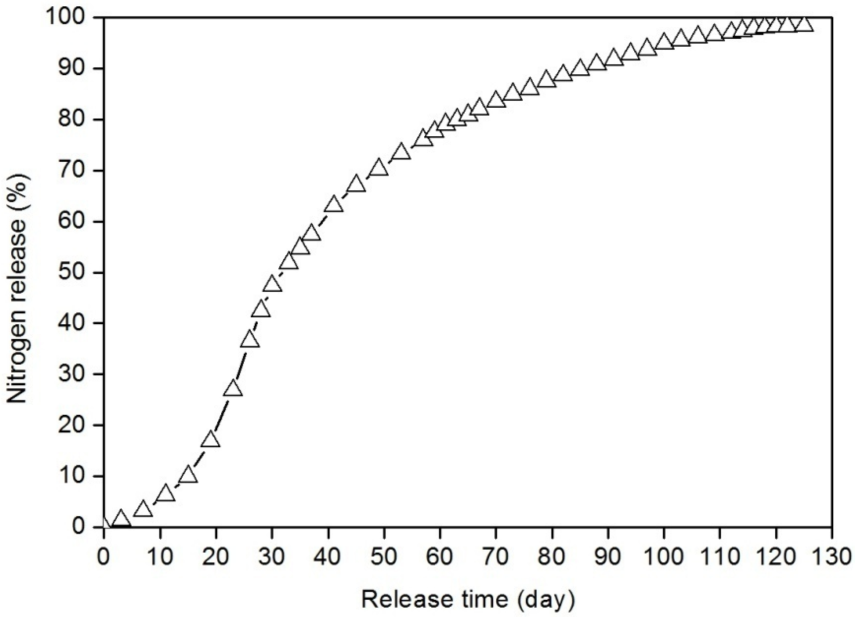


Figure 3.15. Nitrogen release profile of NCU

In other words, the lag can be due to the time needed for the establishment of a steady state between the flux of water entering the granule and the flux of solute leaving it. Once a steady state is achieved the volume change in the granule is negligible.

Starting from 20th day the release percentage rises rapidly and reaches to 89.65% at the end of 85th 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 85th day to 125th day and the amount of nitrogen release reaches 98.27% at the end of the 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.

From the experimental data, a regression model is applied to the nitrogen/nutrient release profile from NCU and the following quadratic equation 3.3 is obtained:

$$y = 0.229\,x^2 - 1.5827x + 1.9284 \qquad ; \ R^2 = 0.9987 \qquad (3.3)$$

Where, x and y represent the release time in days and nutrient in form of nitrogen release (%) respectively.

The experimental data for nitrogen release from NCU was also compared with the Nitrogen release data available from the literature for other CRCU such as ACU (Agrium coated urea), LTPCU (Large tablet polymer coated urea) and MPOCU (Modified polyolefin coated urea) and the results are shown in figure 3.16 [76, 107, 143].

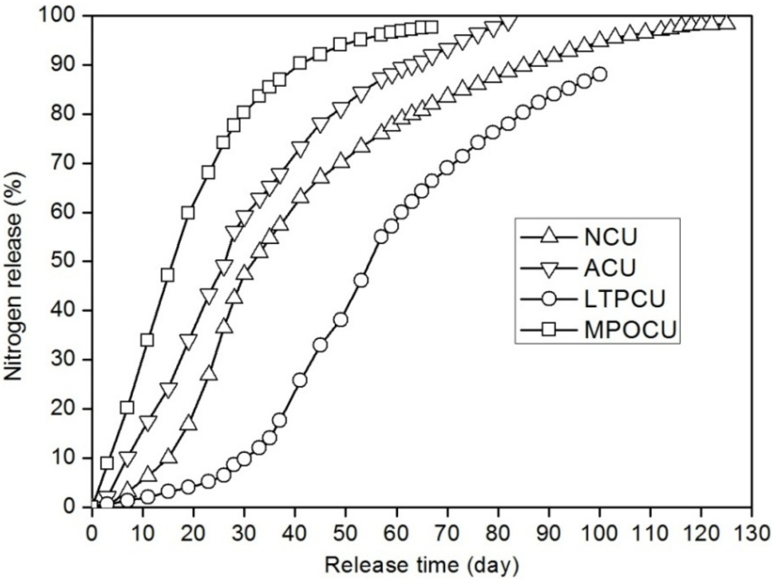


Figure 3.16. Comparison of nitrogen release in NCU with other Coated Urea

From figure 3.16 we can infer that neem coating is effective in increasing the release time of nutrient from urea as compared to other coating materials since for achieving a representative 90% release the time taken is 40 days (MPOCU), 65 days (ACU), 90 days (LTPCU) and 100 days for NCU, thus NCU imparts a better controlled release character to the urea along with the added advantage of coating being biodegradable.

Also the nutrient release from NCU (figure 3.15) is in agreement with three criteria established by the CEN [12] as described in section 1.7.2. CEN defines the conditions for a fertilizer to be described as slow-release if the nutrient or nutrients declared as slow/controlled release meets defined conditions as shown in table 3.6 at a temperature of 25^{o}C. The comparison of NCU experimental data with CEN criteria is tabulated below

Table 3.6. Comparison of experimental data with CEN Criteria

S. No.	**CEN Criteria**	**Experimental results from NCU**
1.	No more than 15% released in 24 hrs	In 24 hrs, percent of nitrogen released is 1.47% which less than 15%, so first criteria is satisfied.
2.	No more than 75% released in 28 days,	After 28 days, percent of nitrogen released is 44.44%, which is less than 75%, so second criteria is satisfied.
3.	At least about 75% released at the stated release time	Amount of nitrogen release is 98.27% within 125 days so third criteria is satisfied.

The nitrogen release rate is also calculated and is shown in figure 3.17. The release rate increases and reaches a maximum at 30 days. After attaining the maxima the release rate decreases and becomes 0.75% /day at about 125 days. The release profile is comparable to the release pattern as shown by other CRCU as shown in figure 3.18.

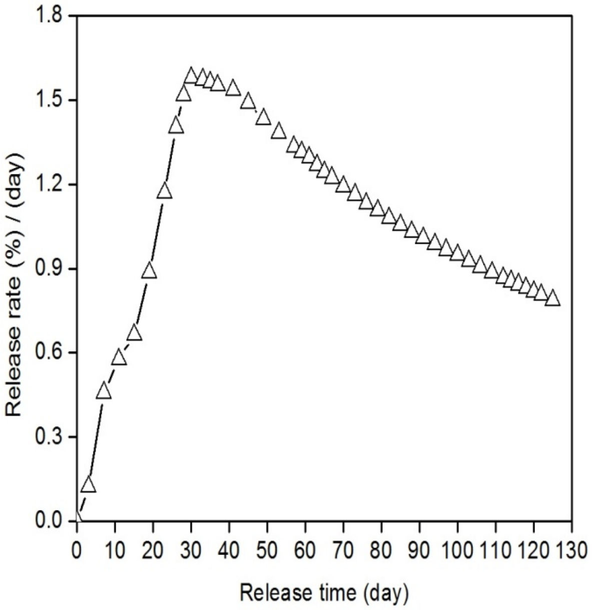


Figure 3.17. Release rate profile of NCU

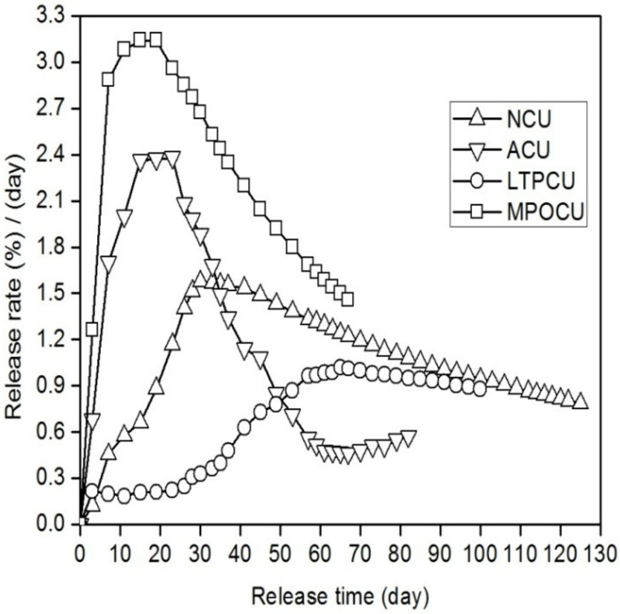


Figure 3.18. Comparison of release rate profile of NCU with other CRCU

3.3.2 Experimental study of nutrient release from NCU by refractive index method

In order to validate and compare results another experimental method based on determination of refractive index (RI) can also be used to measure the concentration of urea in solution directly and thus provide a fair estimate of nutrient release from the sample. This method offer distinct advantages like fast analysis, high efficiency, free from chemical or reagent consumption.

In the present work the percentage of Urea release in terms of nitrogen content and refractive index values for NCU was measured and compared with UCU and also with literature values for other CRCU like polymer coated urea (PCU) and Bentonite (using chitosan as binder) coated urea (BCU) [137].

To determine the nutrient release 50 g of sample (UCU and NCU) were placed in 250 ml distilled water in separate Erlenmeyer flask and sealed. The RI of both the samples was measured using refractometer (Make: ATAGO available at Thermodynamics Research Lab in Malaviya National Institute of Technology Jaipur) as shown in figure 3.19 to get the nutrient release in the solution.

Figure 3.19. Refractometer used in RI determination experiments

The instrument was calibrated daily before measurements against a known RI of water and RI of urea samples were measured at 25^{o}C and 40^{o}C as a function of time for 3, 7, 11, 15, 19, 23, 26 and 30 day. The value of RI is related to the concentration of urea dissolved in water. Figure 3.20 presents the NCU calibration curve in distilled water constructed with standards from 0 to 250000 ppm at 25°C and 40°C. The two temperatures are selected to see the effect of temperature on release mechanism. The curve depicts linearity over a wide range, which helps in the measurement of nutrient release from NCU without dilution of samples.

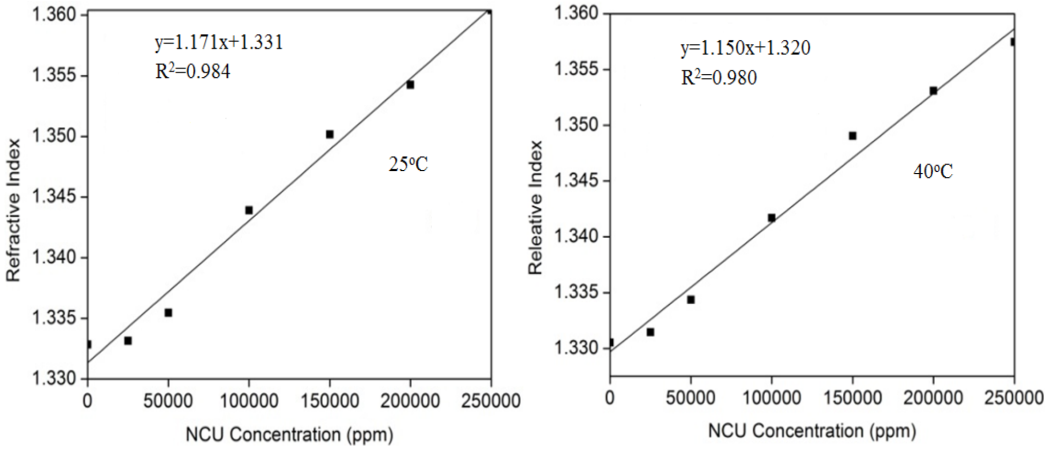


Figure 3.20. Calibration curves for NCU at different temperature

The RI values for NCU at 25°C and 40°C and corresponding nutrient release percentages (using the calibration curves) are plotted in Figure 3.21 (a) and 3.21 (b) respectively. The nutrient release rate increases with increases in temperature. This fact was also shown by dissolution test explained earlier. This temperature dependency helps in ascertaining the urea availability to the crop as per ambient and corresponding soil temperature.

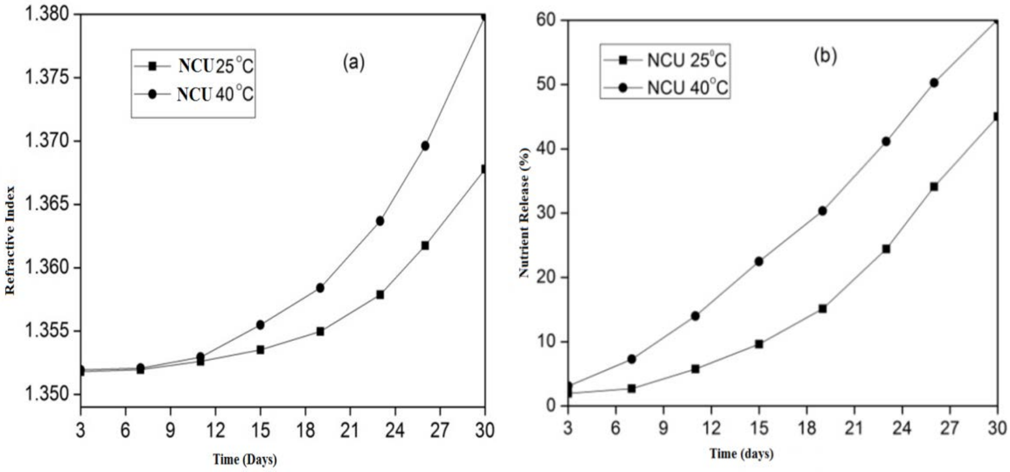


Figure 3.21. NCU (a) Refractive Index Values (b) Nutrient release percentage

In order to compare the controlled release efficiency of NCU with UCU and other CRCU such as PCU and BCU the measured/literature RI values and nutrient release percentages at 25^{o}C were compared. The results are shown in figure 3.22 (a) and (b) respectively and also listed in table 3.7.

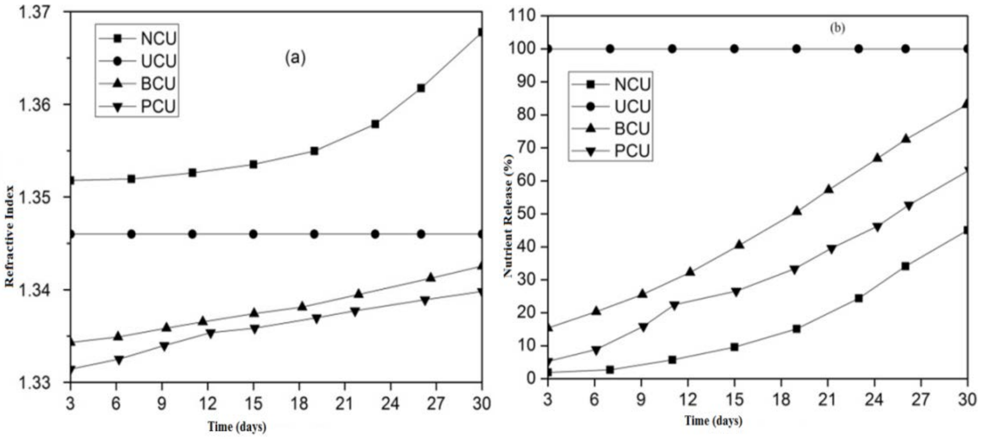


Figure 3.22. UCU, BCU, PCU and NCU (a) RI values (b) Nutrient release percentage

The results shows that 1.03, 4.0 and 4.8 % Nitrogen of NCU, PCU and BCU, respectively were released into the water during the first day and the values at the day 30 were 45.03, 63.4 and 81.9%, for NCU, PCU and BCU respectively. On the other hand the uncoated urea released all its nitrogen content within one hr. Also in case of NCU the percentage nutrient release determined by RI method matches with UV-Vis spectrophotometer method. So RI method was done for 30 days and then further determination was not carried out since percent release from both methods matched for 30 days determination and percent release data beyond 30 days was already available from UV-Vis spectrophotometer method.

Table 3.7. Nutrient Release of UCU, NCU, PCU and BCU

Sample	**Nutrient Release (%)**	
	1 day	**30 day**
UCU	100	100
NCU	1.03	45.03
PCU	4	63.4
BCU	4.8	81.9

These release data shows the slow release properties of NCU, PCU and BCU samples which also follows the CEN standards (as explained in section 1.7.2). Also release from NCU is slower for any particular time as compared to PCU and BCU; this indicates better control over nutrient release when urea is coated with Neem oil. So NCU performed better than other CRCU, in terms of its controlled release behaviour apart from neem oil being biodegradable and also acting as biopesticide and insecticide.

3.4 Rapid technique for determination of nutrient release from NCU in water domain

Since release from CRF may span over many days to several months depending on the coating specification and duration of crop growth, so a rapid technique is needed to verify the label specifications of nutrient release rate and duration.

Although coating can be applied on any nutrient granules, much of the interest and justification for coating is on nitrogen (N) source [144, 145]. Verification of nutrient release pattern of CRF is critical for evaluation of effectiveness of these fertilizers for supplying plant nutrients according to the crop needs and the duration of crop growth. Despite a variety of prediction models and methods to evaluate the nutrient release [38, 146-150] being developed in the past, there is no consistent and standardized method being recognized to date [150-152].

Most of the nutrient release predictions rely heavily on the characteristics of the coating materials but nutrient release of CRF is predominantly temperature dependent [145, 153-156]. Thus, an alternate approach is desirable to establish a correlation between the nutrient release and temperature. This correlation can be used to predict the rate and duration of nutrient release at ambient temperature by using the nutrient release measurement over a short duration at high temperature.

Researchers [157-159] evaluated the nutrient release pattern from two resin-coated N, P, K fertilizers at 25^{o}C, 50^{o}C, 60^{o}C, 70^{o}C, 80^{o}C and 90^{o}C. They suggested that calibration of nutrient release at 80^{o}C and 25^{o}C can be used to predict the nutrient release rate at 25^{o}C (in days) using the release results at 80^{o}C (in hrs).

Using this line of suggestion, in the present work a rapid test for prediction of nutrient release at 25°C from NCU is presented using the nutrient release data at 100°C temperature and also a comparison with the data available for nutrient release from PCU is done.

As per procedure outlined in section 3.3.2 (using refrectometer with temperature control) the nutrient release rate was determined from NCU at 25°C and 100°C. The experiment ends when nutrient release percentage reaches 98.35% at 25°C for 126 days. Similar process was used at 100°C and the experiment ends when for the nutrient released is 100% for 245 hrs. Two repetitions were performed in the release test for the sake of attaining accuracy in the results.

From experimental results we can infer that time period for about 98% release of nutrients at 100°C lies within the range of several hrs or few days as against that of several days or months for similar magnitude of nutrient release at 25°C. So, a calibration between the nutrient release rates at 100°C and 25°C can be utilized for prediction of nutrient release rate at 25°C by finding the release rate at 100°C. This can be carried out as follows:

(1) Nutrient release rates in water from NCU at 100°C and 25°C are determined experimentally using refractive index measurements, until at least 98% of total nutrients are released at both temperatures

(2) A relationship between the cumulative nutrient release as percent of total nutrient present in the product (P) and time (T) at each temperature is suggested as :

$$P_1 = a_1 + b_1T_1 + c_1{T_1}^2 \tag{3.4}$$

Here

P_1 : cumulative nutrient release at 100˚C,

T_1 : release time expressed in hrs,

a_1, b_1, and c_1 are constants, similarly

$$P_2 = a_2 + b_2T_2 + c_2{T_2}^2 \tag{3.5}$$

Here

P_2 : cumulative nutrient release at 25˚C,

T_2 : release time expressed in days,

a_2, b_2, and c_2 are constants.

(3) Using above equations, the time needed for nutrient release of different percentages (R_1, R_2, R_3, R_4 and R_5 etc.) of total nutrients as N_{21}, N_{22}, N_{23}, N_{24} and N_{25} etc. in days at 25^oC; and N_{11}, N_{12}, N_{13}, N_{14}, and N_{15} etc. in hrs at 100^oC are found.

It is noteworthy that the percent of total nutrient that is released is similar for a given pair of release times at two different temperatures, i.e., N_{21} and N_{11}, N_{22} and N_{12} and so on.

(4) Above paired values can be used to develop a relationship between the nutrient release and release time at 25^oC as a function of that at 100^oC as follows:

$$N_2 = U + VN_1 + WN_1^{\,2} \tag{3.6}$$

Here

N_2 : release time in days at 25^oC,

N_1 : release time in hrs at 100^oC,

U, V and W are the constants

(5) The same steps were also followed for nutrient release determination from PCU using data available in the literature [160]

Thus, knowing the nutrient release time at 100^oC for a particular value of the percent release of nutrients from an unknown CRF, one can conveniently obtain the release time at 25^oC for the same percent release.

3.4.1 Nutrient release characteristics of PCU and NCU at 25˚C and 100˚C

As shown in figure 3.23 at 25˚C percentage of nutrient that is released out of total available from PCU is 47.95% and that from NCU is 98.35% over a period of 126 days. Also as shown in same figure at 100˚C, complete (100%) nutrient release from PCU occur in 165 hrs, this was less than that from NCU (245 hr).

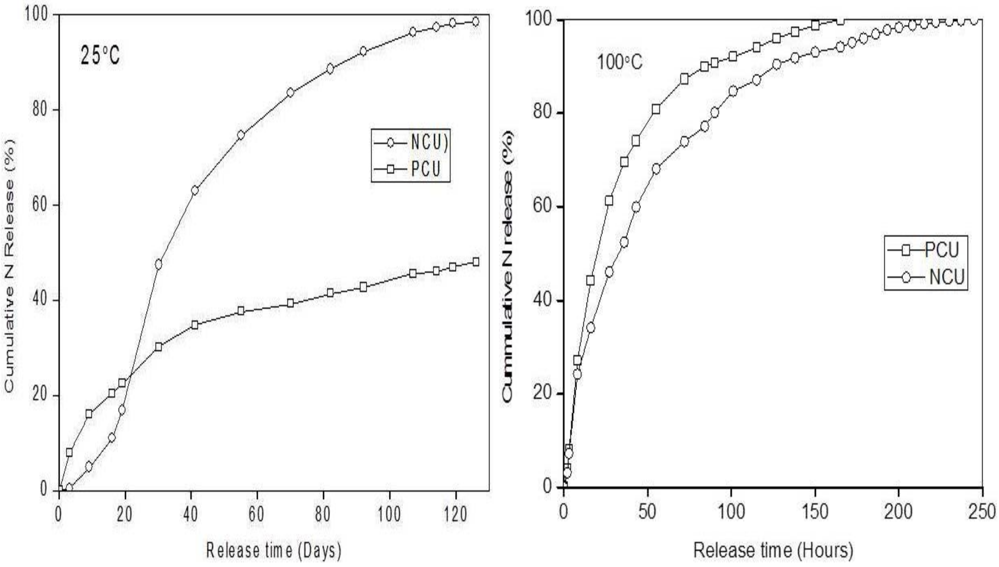


Figure 3.23. Cumulative Nutrient release as percent of total nutrient from PCU and NCU in water at 25˚C and 100˚C

3.4.2 Predicting total nutrient release at 25˚C using measured value of release at 100˚C

A polynomial function can be used to express empirical relationship between cumulative nutrient release percentage and release time at 25˚C and 100˚C for both the chosen CRCU material *viz.* PCU and NCU (Table 3.8).

Table 3.8 Relationship between P_1 and P_2 and time expressed in days (T_2) for 25˚C and in hrs (T_1) for 100˚C, and empirical equations to determine nutrient release at 25˚C using the release time at 100˚C for any given release percent

CRCU Type	**Temp.**	**Cumulative percent release of total Nutrient release as a function of Time**	R^2	**Empirical relation between Release time at 25 ˚C expressed as a function of that at 100˚C**	R^2
PCU	25°C	$P_2= -8*10^{-7} T_2^4+0.003 T_2^3-0.0327 T_2^2+1.7755 T_2$	.9946	$N_2=0.1736 N_1^2+4.5813 N_1-18.976$	.9991
	100°C	$P_1= -7*10^{-7} T_1^4+0.003 T_1^3-0.0471 T_1^2+3.2929 T_1$	.998		
NCU	25°C	$P_2=8*10^{-10} T_2^6-4*10^{-7} T_2^5+6*10^{-5} T_2^4-0.0054 T_2^3+0.2027 T_2^2-1.2379 T_2$	.9978	$N_2=-4*10^{-5} N_1^4+0.0052 N_1^3-0.1994N_1^2+3.3513 N_1+4.6007$	.9847
	100°C	$P_1= -10^{-11} T_1^6+10^{-8} T_1^5-4*10^{-6} T_1^4+0.0006 T_1^3-0.0509 T_1^2+2.7736 T_1$	.9983		

The regression equations obtained above are highly significant with $R^2 > 0.99$. Using the above obtained regression equations, the time needed for obtaining different nutrient release percentage was calculated at both 25˚C and 100˚C (Table 3.9). The N_1 and N_2 values for PUC and NCU so obtained were utilized to establish regression equation between release time at 25˚C as a function of that at 100˚C for both CRCU types (PCU and NCU) as given in Table 3.8.The regression equations in this case are also highly significant with values of $R^2>0.99$.

Table 3.9. Calculated time obtained using equations and for different cumulative nutrient release (as a percent of total Nutrient available) for PCU and NCU

Cumulative percent release of total Nutrient release as a function of Time	**Time required for release as indicated**			
	PCU		**NCU**	
	100˚C	**25**˚C	**100**˚C	**25**˚C
	Hrs	**days**	**hrs**	**days**
8	2.11	3.48	13.05	3.81
15	8.19	5.17	18.61	4.69
26	24.08	7.78	22.41	10.11
38	62.27	12.07	26.15	20.52
47	115	17.47	29.34	30.13
55	175.12	22.51	35.62	39.18
60	204.13	25.2	39.12	42.97
	N_1	**N_2**	**N_1**	**N_2**

3.4.3 Application of rapid method to predict total nutrient release at 25˚C

Starting from an unknown coated fertilizer having some resemblance in terms of coating characteristics, a rapid release test can be done at 100˚C. The release time to obtain a given nutrient percent of total nutrient at 100˚C can then be substituted in either of the equation in Table 3.8 (pertaining to PCU or NCU) to obtain the time required to release the similar percentage of total nutrient at 25˚C. Hence the nutrient release percentage at 25˚C can be conveniently and accurately predicted by utilizing the rate 100˚C.

Unlike the earlier available methods of prediction of nutrient release from CRF products, the method described in present study is rapid, reproducible and does not use or require chemicals for analysis. Therefore, the proposed methodology can be easily applied both by the fertilizer manufacturers and distributors for accurate estimation of CRF release rate and duration.

3.5 Experimental determination of nutrient release from NCU in soil domain

Traditionally, the nutrient release from CRF is determined using a static test in which the CRF (in present case NCU) is dissolved in water and the method of spectrometry or refractometry (as explained in section 3.3.1 and 3.3.2) is used to analytically determine the release behaviour. These laboratory measurements are often used by manufacturers to inform the end users regarding the nutrient release characteristics, although the results of these methods suffer from inherent defect of having a lack of correlation between the results obtained from the field measurements [161]. One such reason for this variation in nutrient release behaviour can be attributed to the fact that the release in soil is concerned with the movement of nutrients not only within soil water but also in the soil matrix.

Although various researchers have put forward different nutrient release techniques but still no standard method exists. For example Simonne and Hutchinson [162] applied the pot-in-pot method in field to determine the number of days in which a specific amount of applied nitrogen can be recovered. The leachate samples collected in the lower pot were analyzed for recovered NO_3-N and NH_4-N. However the most common technique involves enclosing a known amount of CRF in porous/mesh bags and bury them in the soil. These mesh bags are subsequently removed after a particular time duration to determine nutrient release. Although variations creep in due to the differences in material being used in mesh bags and the determination techniques employed for finding nutrient loss. For instance, a proper enclosing material should allow the CRF to be exposed to soil and the same moisture conditions that affect the intended crop. A mesh bag material with too small hole openings may inhibit the CRF exposure to soil, whereas one with large openings may lead CRF to fall out of the enclosure. Pack et.al [163] used cheesecloth and then ground the PCU prills to dissolve the remaining urea in a known amount of water. The solution was then analyzed by total Kjeldahl nitrogen (TKN) method. Gandeza et al. [164] and Zvomuya et al. [122] used plastic mesh and directly analyzed the prills by TKN. Savant et al. [165] and Salman et al. [166] used nylon screen and determined the loss of urea by the loss of weight from the prills. In most of the weight loss techniques the percentage of nutrient released from a CRF was determined using chemical analysis, which can be expensive and time-consuming.

In the present study nutrient release characteristics of NCU in soil are obtained using two methods: (a) weight loss method and (b) chemical analysis method. The results so obtained for NCU are compared with the literature data available for release characteristics of Agrium PCU (APCU) (produced and marketed by Agrium Inc. US) under same conditions[128]. Also nutrient release from NCU in soil is compared with that in water domain.

The details and results of the two methods are explained below:

3.5.1 Weight loss method

The study was carried out at Agriculture research station, Durgapura, Jaipur. In the weight loss method sealing bags made of polypropylene mesh with 1.2 mm^2 hole openings and a 43% open area are used. Mesh bags of dimensions 10 cm x 10 cm and heat-sealed with an impulse sealer along three edges are used in experiment. In each bag 3 ± 0.0002 g of NCU were placed and then the open side was heat-sealed. The experiment had three replicates. Each replicate consisted of 8 bags that were buried in the sandy clay loam soil of the experimental area 10 cm below the surface and watered twice a week in order to maintain the field capacity. The experiment was carried out in a complete randomized design and analyzed statistically as per procedure suggested by [167]**.** During the experiment, one mesh bag was retrieved from each replicate at 15 day’s intervals up to 120 days after incubation (DAI). The time limit of 120 days was chosen to make a fair comparison with the analytical technique results for nutrient release in water domain explained in earlier sections. NCU prills from the mesh bags were air dried for a minimum of 14 days before processing. The prills were then removed manually from each mesh bag, separated from soil, and then weighed. To determine the nutrient release percentage, first the weight of the neem oil coating in 3 g of NCU was determined using the following equation:

$$\mathrm{F_c} = \mathrm{F_i} - \left[\frac{\mathrm{F_i} * (\%\mathrm{N_{NCU}})}{\%\mathrm{N_{UCU}}}\right] \tag{3.7}$$

Here,

F_C : weight of the neem oil coating in grams,

F_i : initial amount of NCU in the mesh bag,

$\%N_{NCU}$: percent of N in the NCU,

$\%N_{UCU}$: percent of N in uncoated urea

Based on data given in table 3.2, the weight of neem oil coating in 3 g of NCU was calculated to be 0.172 g. From literature, for APCU this value is 0.13 g [128]. The %NR (percent nutrient release) for each sampling date was then obtained using following equation:

$$\%NR_W = \left[1 - \left(\frac{F_s - F_c}{F_i - F_c}\right)\right] \times 100 \tag{3.8}$$

Here

$\%NR_W$: percent of N release as determined by the weight method,

F_s : weight of the NCU on the sampling date,

F_c : weight of the neem oil coating (determined using equation 3.7),

F_i : initial amount of NCU in the mesh bag

3.5.2 Chemical analysis method

In the second method, %NR was determined by chemical analysis. NCU prills from each sampling date were air-dried, crushed in a mortar and pestle, and then N was determined using a combustion analyzer following the general methods for plant material in Horneck and Miller [168]. The N found by combustion was multiplied by the weight of the NCU sample to determine N content remaining in granules. The %NR for each sampling date was then determined by the following equation:

$$\%NR_C = \left[1 - \left(\frac{N_s}{N_i}\right)\right] \times 100 \tag{3.9}$$

Here

$\%NR_C$: percent of N release as determined by the chemical method,

N_s : N content in grams of the NCU on the sampling date,

N_i : initial N content in 3 g of NCU as determined by combustion

The actual N concentration in the NCU granules on Day 0 before mesh bag burial was 43.79 % ± 0.2%. For APCU from literature it is 44.5% ± 0.2% based on chemical analysis.

The experimentally determined nutrient release % (averaged over different runs) using both methods for NCU are tabulated below:

Table 3.10. Experimentally determined average nutrient release % for NCU

DAI (Days)	Nutrient release (%)	
	By Weight Method	**By Chemical Method**
15	10.2	8.6
30	43.1	39.5
45	63.4	59.6
60	73.5	70.1
75	79.6	75.6
90	86.9	83.2
105	91.1	88.6
120	93.7	90.8

The nutrient release % for both methods for APCU as obtained from literature is tabulated below. Data extraction from literature plots is done using webplot digitizer 2.0.

Table 3.11. Nutrient release % for APCU as obtained from literature[128]

DAI (Days)	Nutrient release (%)	
	Weight Method	**Chemical Method**
15	4.8	2.5
30	12.4	11.3
45	39.4	38.4
60	57.2	55.3
75	78.2	73.2
90	85.7	82.3
105	92.6	89.8
120	94.8	91.6

3.5.3 Results for nutrient release in soil

In order to establish the association between the two methods of calculating %NR, correlation coefficients were calculated using MS-Excel and a regression line was fit to the data for both NCU and APCU. From figure 3.24 it is observed for both NCU and APCU the correlation coefficients are found to be 0.999 and the slope of the regression line was also found to be near 1. This indicates that the %NR on each sampling date was approximately in 1:1 ratio, which also means that predicted %NR by each method was similar at every sampling date.

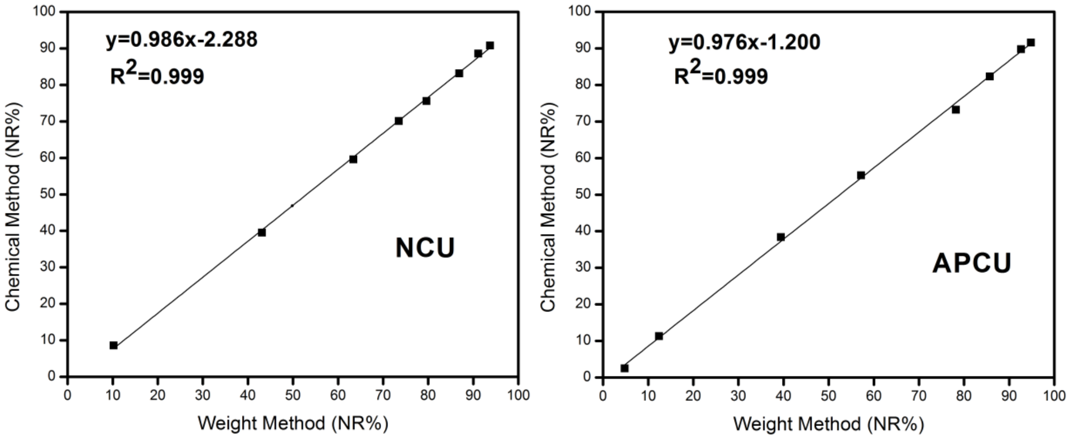


Figure 3.24. Correlation between two different methods for determining %NR for NCU and APCU) incubated at depth of 10 cm in soil. Each point represents one paired observation

To explore nutrient release behavior using each method % NR is plotted as a function of DAI for both NCU and APCU (as shown in figure 3.25). The release behavior depicted a sigmoidal stage wise trend in both CRF. % NR peaked at 85% at around 100 DAI. After this decay stage sets in because the fertilizer cannot release more than 100%.

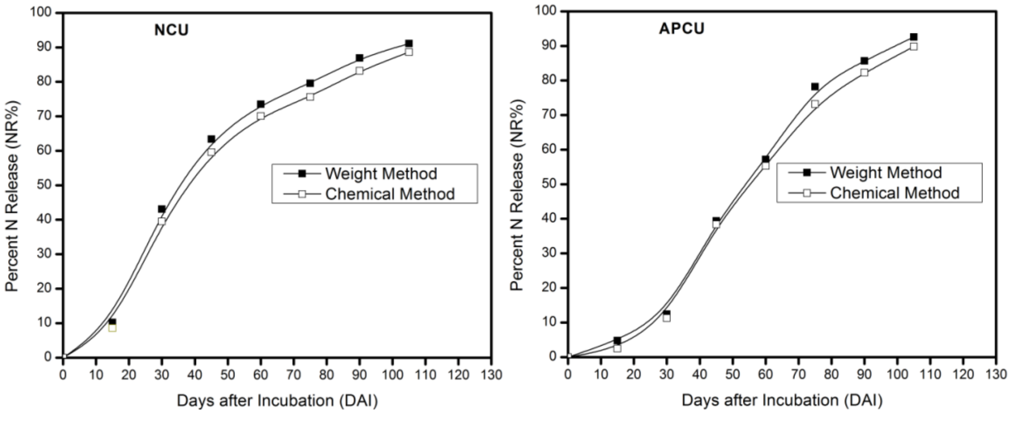


Figure 3.25. %NR as a function of DAI for NCU and APCU

Both methods resulted in similar %NR over time for the two different types of CRF. This establishes the fact that the weight method can be considered a good predictor of nutrient release for the CRF under test. Also weight method is cost effective since no chemical reagents and analytical equipment is needed. Although in some coatings on CRF there is potential to retain water even after sample being thoroughly air-dried, due to which some error can occur in the weight determination and thus %NR. However, no such problem is encountered in the present study.

3.5.4 Comparison of nutrient release behavior for NCU in soil and water domain

The nutrient release behavior of NCU in soil and water domain (at 25^{o}C) is compared in figure 3.26. The data for water domain was obtained from spectrometry method (section3.3.1) and for soil domain using weight method (as given in previous section). From figure 3.26 it can be inferred that the release in sand (soil domain) was slower than in water, clearly indicating that environmental properties contribute to the restriction of nitrogen release. However, the difference of release in sand and water is not very large. This shows that the main controlling factor for nutrient release is the coating layer itself and not the external environment that surrounds the coated fertilizer, be it water or sand.

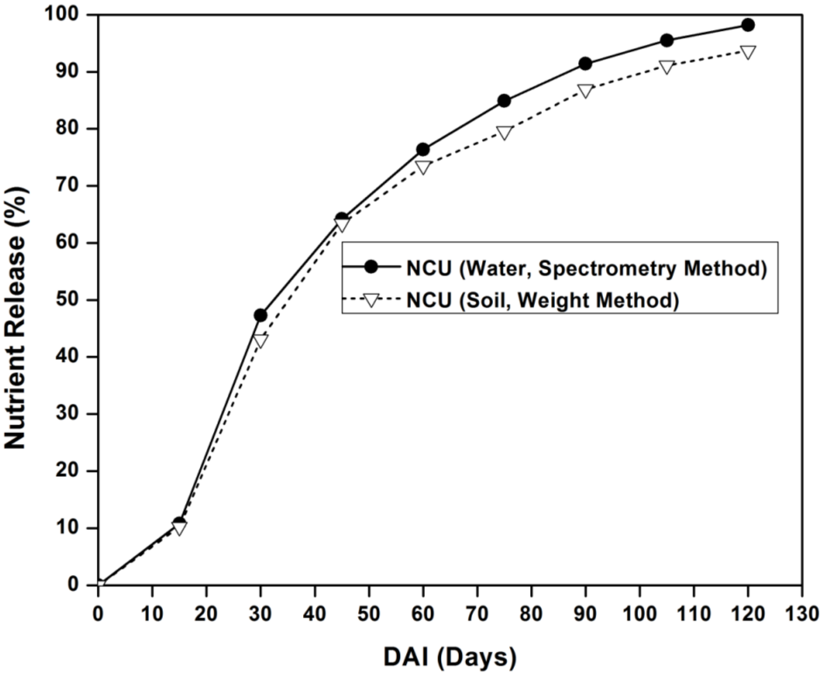


Figure 3.26. Comparison of nutrient release for NCU in water and soil domain

CHAPTER 4

Modelling and Simulation of Nutrient Release from NCU with Perfect Coating

In the previous chapters significance of CRCU in general and NCU in particular are presented unveiling its controlled release behaviour and hence its importance in enhancing nitrogen use efficiency by plants leading to improved crop yields and also controlling environmental pollution by reducing hazardous gaseous emissions and water eutrophication. Parametric analysis of the release behaviour of CRF is vital for design and development of new CRF. However, the experimental approaches suffer from obvious disadvantages of being time consuming, cumbersome and expensive. So, mathematical modelling and simulation techniques to evaluate the nutrient release behaviour comes handy in developing a understanding of release dynamics and also in design of new CRF in a shorter time span and at a relatively lower cost. Thus in present chapter modelling and simulation of nutrient release from a single granule of NCU is presented.

In present study a multi diffusion model is developed to predict nutrient release from NCU whereby explaining the sigmoidal three staged controlled nutrient release behaviour. Model is developed for multilayer including the neem oil coating, water domain and it couples the finite element approximation with 2D geometry, also to improve the accuracy of simulation urea diffusivity in water is taken as a function of its concentration. 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/soil environment. To check reliability and robustness of the model, experimental results (taken from the literature) of nutrient release from other CRCU differing from NCU in core and coating thickness are compared with the model predictions.

In the present chapter various aspects of mathematical modelling and related results for the ideal case of perfect neem oil coating on urea core are discussed. Section 4.1 presents the mathematical model development for staged nutrient release behaviour under given boundary conditions. Section 4.2 presents the model verification using the experimental data of nutrient release from NCU. Section 4.3 discusses the effect of coating thickness on nutrient release from NCU in water domain. Section 4.4 presents the effect of core radius on nutrient release from NCU. Section 4.5 presents the comparison of model results with literature data of other CRCU for testing reliability of model. Section 4.6 discusses the simulation results in 2 dimensional (2D) for nutrient release from NCU.

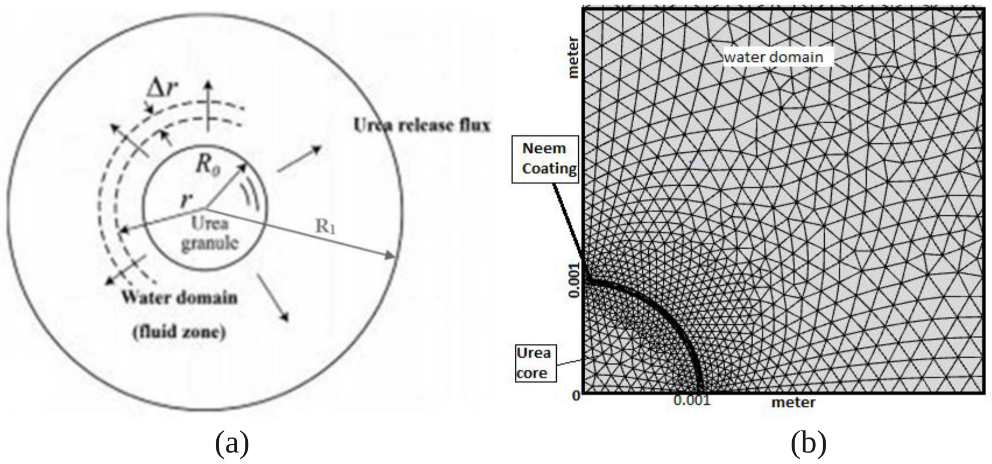
4.1 Development of mathematical model

Glaser et al. studied the release from PCU and applied one-dimensional coordinate diffusion system [169]. 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 also not included [170]. Lu and Lee applied the Fick’s law in spherical coordinate for the release from latex coated urea (LCU) [142]. Al-Zahrani modelled unsteady state release from polymeric membrane particle and assumed a well-mixed condition inside sphere particle [171]. Majority of the modelling studies for CRF 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 PCU 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 [141].

Application of finite-element method (FEM) for modelling of nutrient release from CRF has been used since 2003 [172]. However, the geometry used in their model was not a particle type specific. Trinh et. al [173] 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 from NCU and other CRCU using a multi diffusion model.

The dissolution model of a perfectly spherical NCU granule surrounded by a water zone is shown in figure 4.1 (a). The NCU granule is divided into two regions viz. urea core (radius=R_0) and Neem oil coating (thickness = a). 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 plausible reason for the occurrence of lag period is that some time is required to fill the internal voids of the NCU granule with a critical water volume.

The present model assumes that the coating layer was saturated with water at time (t_0) of initial release. Water inside the core starts dissolving the solid urea where urea concentration is kept at the saturated level till solid urea exists in the core. Nutrient in form of nitrogen is released through the coating layer by the diffusion with a constant rate. Thus, it is called “constant release” stage. When solid urea in the core is completely dissolved, urea concentration starts dropping or decreasing and a “decay release” stage sets in which continues till the end of the process.



(a) (b)

Figure 4.1. (a) Dissolution model of a spherical NCU granule in water domain (b) Geometry and mesh generation of a urea dissolution model for NCU in COMSOL

Using the mass transport equation, the transient stage of urea diffusion through the coating layer is represented by equation 4.1 [107].

$$D_{eff}\left[\frac{\partial^2 C(r,t)}{\partial r^2}+\frac{2}{r}\frac{\partial C(r,t)}{\partial r}\right]=\varepsilon\frac{\partial C(r,t)}{\partial t} \tag{4.1}$$

As the urea granule is motionless, so it is pertinent to assume that urea flux emanating from the coating interface to the liquid environment is primarily controlled by the diffusion of nutrient in liquid. Thus, diffusion is calculated on the basis of mass transport equation of nutrient from urea granule in water as follows:

$$D_U\frac{\partial^2 C(r,t)}{\partial r^2}+\frac{2D_U}{r}\frac{\partial C(r,t)}{\partial r}=\frac{\partial C(r,t)}{\partial t} \tag{4.2}$$

Inside the water zone, urea diffusivity in liquid, D_U, varies according to urea concentration as given by equation 4.3 [174].

$$D_U(r,t)=(1.380-0.0782\,C(r,t)+0.00464\,C(r,t)^2)10^{-5}\,cm^2\,s^{-1} \tag{4.3}$$

To solve the model, Finite element method (FEM) and 2D geometry was applied. COMSOL Multiphysics version 5.3 was used to find the nutrient release behavior from single granule. Since NCU granule under consideration is spherical, due to symmetry considerations the model's geometry was applied on one quarter of a sphere. Geometry and meshing for single NCU granule is shown in figure 4.1(b). The fluid zone diameter, i.e. the distance from the centre of NCU granule to the centre to the water boundary (R_1), was set at twenty-two times of the core radius (R_0) [175].

In order to solve equations 4.1-4.3 the PDE was discritized using backward difference formula (BDF). The BDF method used in solution had 10200 degrees of freedom. The model was having 20100 elements with an average mesh quality of 0.9668 after conducting mesh convergence analysis. The error between iterations ranged from 10^{-19} to 10^{-16} during the calculation. The Initial and boundary conditions (I.C’s and B.C’s) used in solution was applied for each stage specifically. The equations used in the present model were as follows:

The total urea mass of a single NCU granule is calculated as follows:

$$M_{\text{Total Urea}} = V_{\text{Core}}\ \rho_{\text{Urea}} \tag{4.4}$$

Here

$M_{\text{Total Urea}}$: total urea mass of the NCU granule (g),

V_{Core} : volume of urea core (m^3),

ρ_{Urea} : density of urea (g/m^3)

The mass of urea that is released as nutrient at any time t is defined as the integral of diffusional flux based at the outer shell of urea particle (r= R_0 + a):

$$M_{Release}(t) = M_{Urea}\ S_{Diff}\ \int_{t=0}^{t} J_{Urea}\ (r,t)\ dt \tag{4.5}$$

The mass of urea present within the urea core is:

$$M_{Core} = M_{Total\ Urea} - M_{Urea}\, S_{Core}\ \int_{t=0}^{t} J_{Urea}\ (R_0,t)\ dt \tag{4.6}$$

Here

J_{Urea} : Diffusive flux of urea (mol m^{-2} s^{-1}),

S_{Diff} : Surface area of diffusion (m^2),

S_{Core} : Surface area of urea core (m^2)

Constant release stage

The concept of lag time (t_0) is already explained and it is obtained experimentally. From time t_0 onwards if the urea solution at the surface of the urea core is saturated and the concentration at the outer layer of the fluid field is zero, then the boundary conditions and initial conditions are given in table 4.1.

Table 4.1. Initial and Boundary conditions

Stage→	**Constant release**		**Decay release**	
Initial Condition	$C_{\text{Const}}(r, t_0) = 0$	$(R_0 \le r \le R_1)$	$C_{\text{Decay}}(r,t_1) = C_{\text{Const}}(r, t_1)$	$(0 \le r \le R_1)$
Boundary Condition -1	$C_{\text{Const}}(R_0, t) = C_{\text{Sat}}$	$(t_0 \le t \le t_1)$	$D_U \nabla C_{\text{Decay}}(R_1, t) = 0$	$(t \ge t_1)$
Boundary Condition -2	$C_{\text{Const}}(R_1, t) = 0$	$(t_0 \le t \le t_1)$		

Here,

C_{Decay} (r, t_1) : 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})

The mass of urea released ($M_{Release}$) and the mass of urea present inside the core (M_{Core}) were calculated using equations 4.5 and 4.6 respectively. In present simulation study, release time is dependent on factors such as amount of urea (shape and size) and the properties of coating material (diffusivity, porosity, thickness). The stage terminates with the complete dissolution of urea core say at time, t_1, when the whole of the urea core is liquefied and saturated with urea.

$$M_{Core}(t_1) = M_{Urea}V_{Core}\ C_{Sat} \qquad (4.7)$$

The above equation 4.7 also gives the end (stop) condition for the constant release stage in concurrence with the model. The end of constant release stage marks the beginning of the decay release stage.

Decay release stage

Decay release sets in with the complete dissolution of solid urea core. The urea concentration within the core shows a perpetual decrease due to the release of urea to the water zone. For this stage the boundary conditions and initial conditions are given in table 4.1.

The urea concentration profile is determined by C_{Decay}(r, t) within the particle. The Urea concentration at urea core at any time t is given by equation 4.8:

$$C_{Decay}(R_0, t) = \frac{M_{Core}\,(t)}{V_{Core}} \qquad (t \geq t_1) \qquad (4.8)$$

As per CEN criteria (section 1.7.2) a good quality CRF releases more than 95% of its urea after the stated time. Also beyond this time the release rates considerably slows down (when $M_{Release}$ (t) reaches closer to $M_{Total\ Urea}$). This leads to a considerable increase in computation time and without any significant improvement in accuracy so following end condition for decay stage is applied.

$$Release\ (\%) = \frac{M_{Release}\ (t_2)}{M_{Total\ Urea}} \times 100\% = 95\% \tag{4.9}$$

4.2 Model verification using experimental data of nutrient release from NCU

In order to estimate the simulation accuracy a mesh convergence analysis was performed as shown in table 4.2. The nutrient release percentage for NCU at time corresponding to transition from constant to decay stage was used to determine the simulation accuracy and establish a proper mesh size for FEM application.

The nutrient release percentage converged to the second decimal place for mesh size factors varying from 0.6 to 1.2 which is in tune with the accuracy obtainable from experimental results. Error between mesh size factor of 0.9 and 1.0 was 0.00125%, hence the factor of 1.0 was used in the model.

Table 4.2. Data for mesh convergence

Mesh size factor	Number of elements	Percent released, %
0.6	34,032	88.00538
0.7	27,824	88.00596
0.8	23,070	88.00545
0.9	20,094	88.00663
1.0	18,292	88.00917
1.1	16,340	88.00404
1.2	14,664	87.75444

The proposed model developed for a single NCU granule whose specific parameters as enumerated in table 4.3 was verified using the experimental data generated from the release test of NCU in water domain as given in section 3.3.1.

To establish the reliability and robustness of the model, a comparison was carried out between the model results and corresponding experimental data obtained from literature for other CRCU. Apart from NCU other CRCU used for validation process include: Modified Polyolefin (MPO1 and MPO2) and latex coated urea (LCU). These chosen CRCU varies in core diameter, coating thickness, as well as release time. The parameters used in model for these other CRCU are also given in table 4.3.

Table 4.3. Parameters used in the model

Type →	**NCU**	**MPO 1**	**MPO 2**	**LCU**
Data Source →	Experimentally Determined	From Literature[141]	From Literature[141]	From Literature[142]
Parameter ↓				
Radius (mm), R_0	1.0	1.2	1.2	7.06
Coating thickness (mm), a	0.0775	0.0375	0.0917	0.353
Lag time, t_0 (day)	19	1.0	5.0	25
Effective diffusivity, D_{eff} (m^2/s)	3×10^{-14}	1.2×10^{-14}	1.2×10^{-14}	39.5×10^{-14}

The standard error of the estimate (SEE) applied to determine the accuracy between simulation and experiment results is evaluated using equation 4.10

$$SEE = \sqrt{\frac{\sum (Y_{Exp} - Y_{Simu})^2}{N}} \tag{4.10}$$

Here

Y_{Exp} : the experimental data,

Y_{Simu} : the simulation results,

N : number of given data

The simulation result for nutrient release from single NCU granule as shown in figure 4.2 corresponded well with our experimental data. The standard error of estimate (SEE) used to determine the accuracy between simulation and experimental 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 that cited in the literature [141, 142, 174, 176].

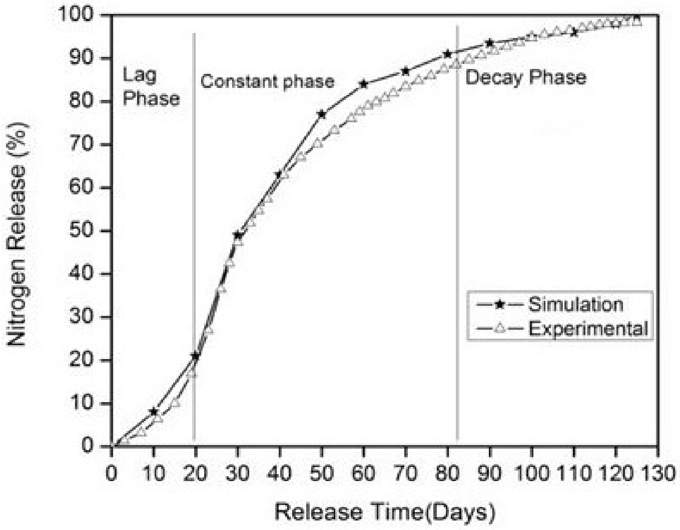


Figure 4.2. Experimental and simulation release profile for NCU

4.3 Effect of coating thickness on nutrient release from NCU

In order to evaluate the effect of coating thickness on nutrient release rate for NCU using the model described above, simulations are carried out for five different coating thicknesses: 0.05, 0.06, 0.08, 0.12, and 0.15 mm keeping core radius (1 mm) and other parameters as listed in first column of table 4.3. The coating thicknesses are chosen on the basis of SEM images obtained for NCU as explained in chapter 3. Diffusive fluxes are plotted against the release time based on the stop condition (equation 4.7) in constant release stage.

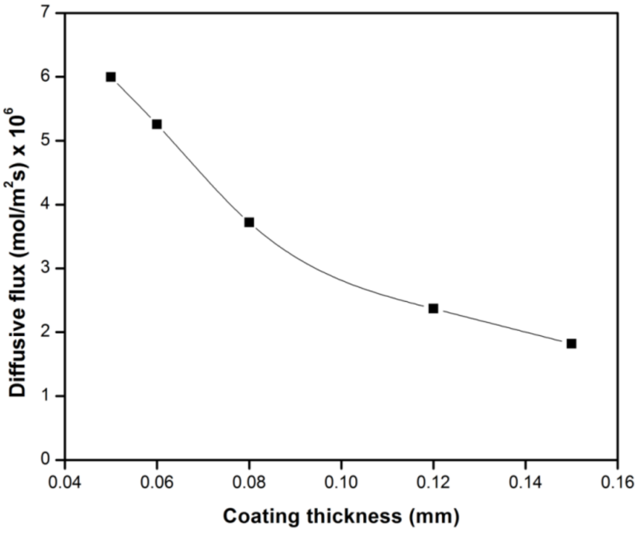


Figure 4.3. Effect of coating thickness on diffusive flux from NCU
(core radius: 1 mm)

Simulation results are shown in figure 4.3 and 4.4 and summarized in Table 4.4.

Table 4.4. Effect of coating thickness on the release of NCU

Thickness (mm)	**Product (R_0 x a)**	**Diffusive flux (mol/(m^2 s) x 10^6**	**Release time (days)**	**Release rate (mol/s) x 10^{10}**
0.05	0.05	5.997	51.612	3.121
0.06	0.06	5.256	61.935	2.820
0.08	0.08	3.72	82.58	2.110
0.12	0.12	2.169	123.87	1.292
0.15	0.15	0.719	154.837	0.3782

From figure 4.3 it is evident that an increase in the coating thickness results in corresponding increase in release time or decrease in diffusive flux, this can be attributed to the fact that the increased coating thickness leads to an enhancement in the diffusion resistance.

An increase in coating thickness also reduces release rate or increase release time as shown in figure 4.4. When coating thickness increase from 0.12 mm to 0.15 mm the release time changes from 123.87 to 154.84 days. So an increase in 0.03mm of thickness leads to a 25 % increase in release time.

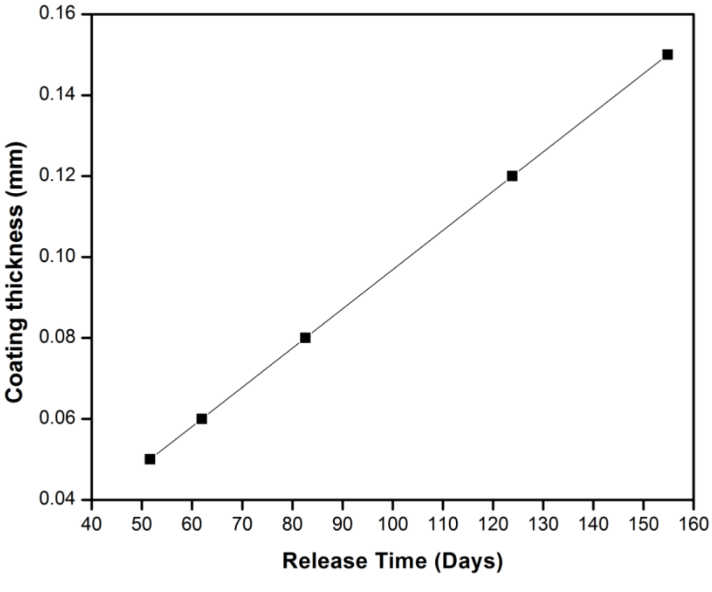


Figure 4.4. Effect of coating thickness on nutrient release time from NCU (core radius: 1 mm)

This point to the fact that an accurate controlled release characteristics is governed by accuracy in coating thickness and particle size to achieve desirable results in terms of release time matching the crop requirement.

4.4 Effect of core radius on nutrient release from NCU

In order to understand the effect of core radius on nutrient release rate for NCU using the model described above, simulations are carried out for five different particle core radius: 1.0, 1.4, 1.7, 2.0 and 2.4 mm while other parameters being used are as listed in first column of table 4.3. The core radiuses are chosen on the basis particle size distribution given in chapter 3. Diffusive fluxes are plotted against the release time based on the stop condition (equation 4.7) in constant release stage.

Simulation results are shown in figure 4.5 and 4.6 and summarized in Table 4.5.

Table 4.5. Effect of core radius on the release of NCU

Core Radius (mm)	**Product (R_0 x a)**	**$\frac{R_0^2}{a}$ (mm)**	**Diffusive flux (mol/(m^2 s) x 10^6**	**Release time (days)**	**Release rate (mol/s) x 10^{10}**
1.0	0.0775	12.903	3.625	80.123	0.4553
1.4	0.1085	25.290	3.634	112.221	0.8943
1.7	0.1317	37.290	3.646	136.657	1.3231
2.0	0.1550	51.612	3.657	160.224	1.8372
2.4	0.1860	74.322	3.662	192.119	2.6490

The Diffusive flux obtained is around 3.6 x10^{-6} (mol/(m^2 s). The release time however varies from 80.123 to 160.224 as the core radius increases from 1.0 to 2.0 mm. Therefore it can be said that the release time varies proportionally with urea core radius. The release rate varies from 0.4553 x 10^{10} mol/s to 2.6490 x10^{10} mol/s as core radius changes from 1.0 to 2.4 mm.

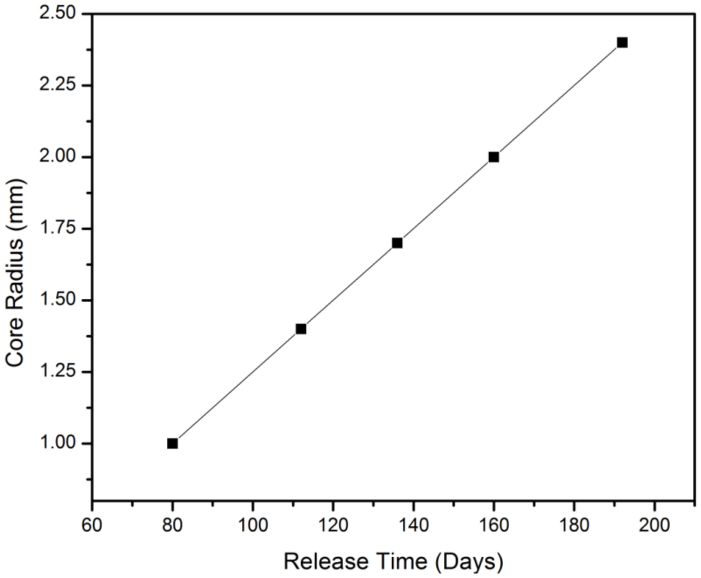


Figure 4.5. Effect of core radius on nutrient release time from NCU (coating thickness 0.0775mm)

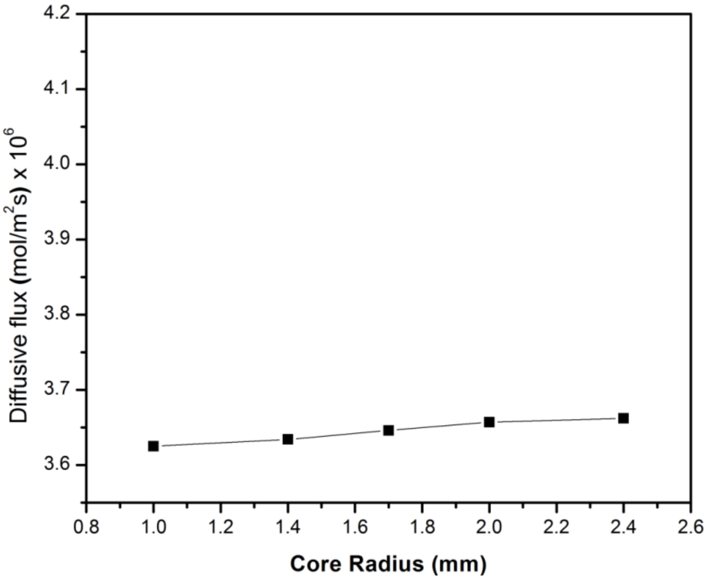


Figure 4.6. Effect of core radius on diffusive flux from NCU (coating thickness: 0.0775mm)

From figure 4.5 and 4.6 it can be inferred that although the diffusive fluxes nearly remain constant with changing core radius but for a given coating thickness the release time increases as urea core radius increases. This can be explained by the fact that an increase in core radius signifies an overall increase in the mass of urea particle. Also the time needed for urea diffusion from neem oil coating is governed by the total amount of urea present in the core. Thus bigger core radiuses gives a higher release time value. So, in order to increase the release time an increase in core radius is a convenient and effective option. This fact is also available in other study which proves the same thing that increasing the core radius of a CRF is more economical and technically feasible [141].

4.5 Combined effect of core radius and coating thickness on diffusive flux and release rate

Shaviv et. al [141] while working on modified polyolefin (MPO) and polyurethane-like coating (PULC) showed that the nutrient release rate varies inversely with the product of core radius (R_0) and coating thickness (a). This implies that core radius and coating thickness have an antagonistic effect on nutrient release rate from CRCU. However according to the present work as shown in figure 4.7 the release rate shows an increases when the product $R_0 \times a$ decreases while varying thickness (a), however changing the core radius (R_0) shows an increase in release rate as the product $R_0 \times a$ increases.

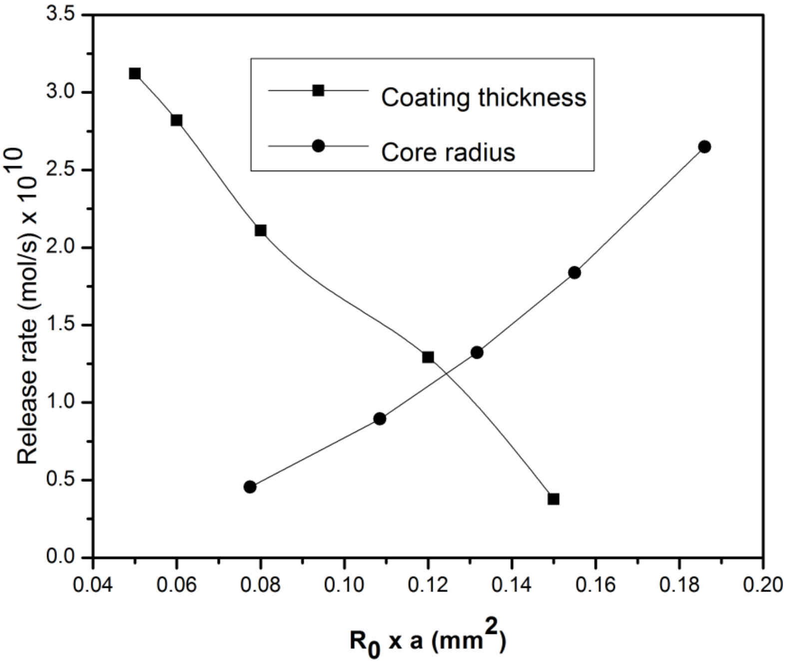


Figure 4.7. Relationship between product R_0 × a with release rate when changing radius or thickness

Using data from table 4.5 a plot (figure 4.8) is made between release rate and R_0^2/a. The regression analysis of data yields a linear relationship which can be mathematically expressed as:

$$Release\ rate = \left(-0.079 + 0.0357\left(\frac{R_0{}^2}{a}\right)\right) 10^{-10}\,\frac{mol}{s} \tag{4.11}$$

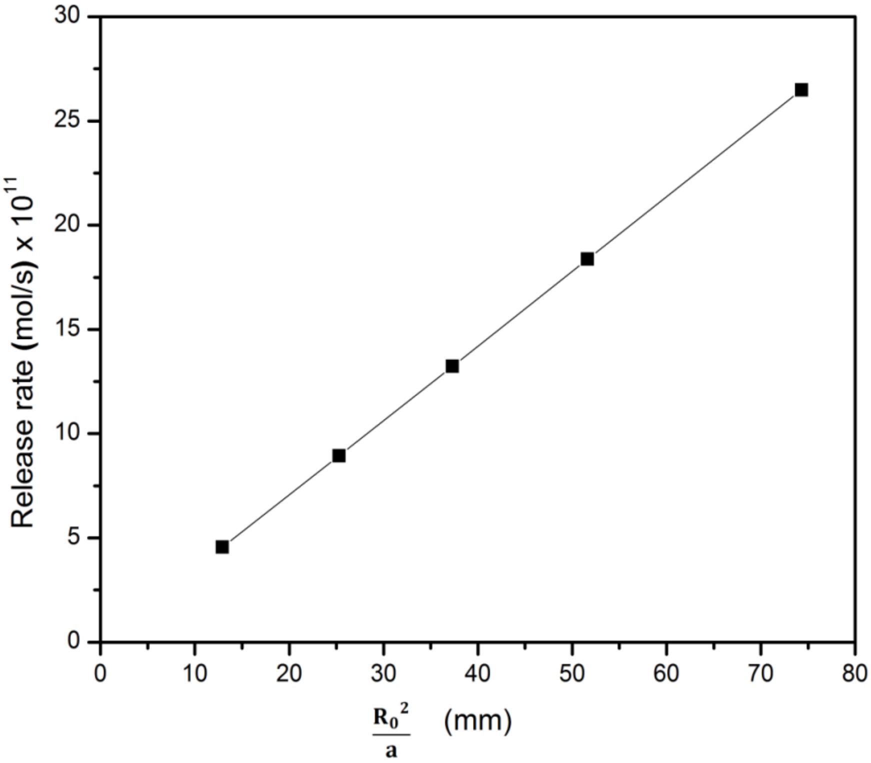


Figure 4.8. Relation between release rate and $\left(\frac{R_0{}^2}{a}\right)$

The above relation is in tune with the diffusion theory of mass transport processes. The relationship shows that release rate varies inversely with the coating thickness and varies directly with the square of core radius. Since diffusive flux is inversely related to coating thickness so release rate also varies inversely with the same. Also the release rate depends on the available surface area for diffusion to take place, which is nothing but equivalent to square of core radius R_0. Thus equation 4.11 provides a better estimate to determine the cumulative effect of core radius and coating thickness on nutrient release rate from NCU in particular and for other CRCU in general during constant release stage.

4.6 Comparison with literature data

To establish the reliability and robustness of the developed model, simulations were done for other CRCU (taken from the literature) data. Simulation runs were done for three samples of two other types of coating material *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. Experimental release data from literature was extracted using webplot digitizer 2.0. The results are shown in figure 4.9.

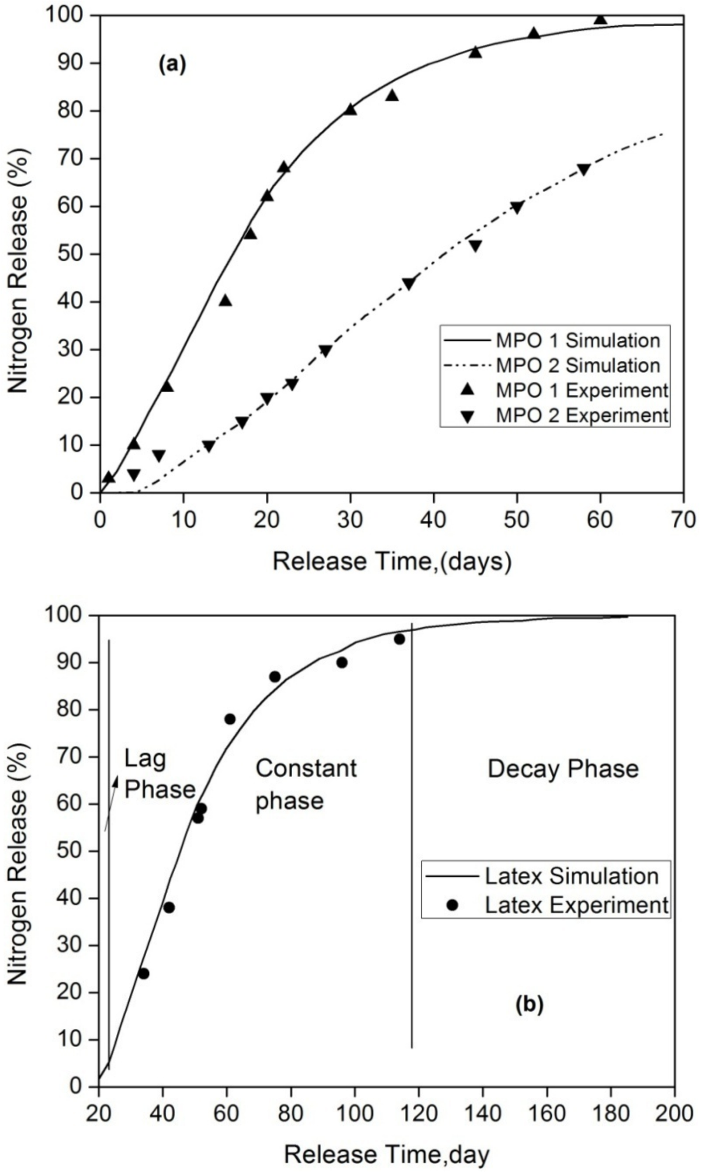


Figure 4.9. Experimental and simulation release profile (a) MPO1 and 2 (b) LCU

Figure 4.9 (a) shows simulation results compared with experimental data from [10] for MPO 1 and 2 where R_0 was taken as 1.2 mm and coating thickness as given in table 4.3. A constant release phase extends upto sixty days in both these case. The SEE ranged from 0.016 to 0.018. Thus, the model satisfactorily predicts the release behaviour and proves to be sufficiently robust in estimating the release for coated urea granules 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 granule where constant phase release time extends upto 120 days which is greater than NCU as shown in figure 4.9 (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.

4.7 Simulation results (2D) for nutrient release from NCU

The three staged nutrient release process from NCU can be more easily understood by COMSOL 2D results as shown in figure 4.10 and 4.11.

The Lag phase or the first phase (t_0 = 19 days) as shown in figure 4.10 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. However during this stage the urea front moves from the core to the surface with no significant release of urea into the water zone. Many previous works have overlooked this phenomenon which is a possible cause for mismatch between experimental and modelling results.

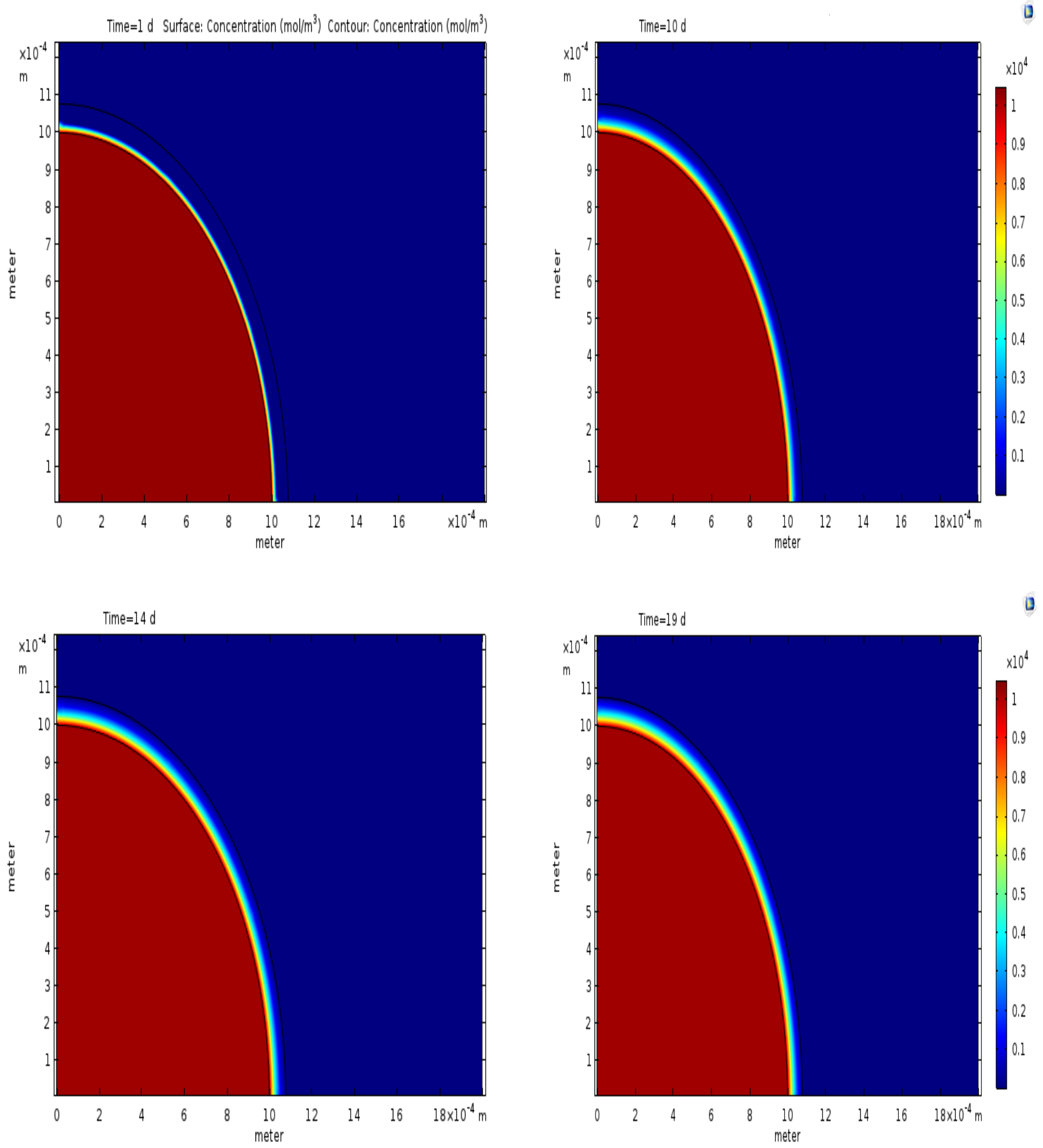


Figure 4.10. 2D release profile in NCU during lag phase. Colour legend represents urea concentration in range of 0-10500 mol/m^3

Figure 4.11 presents results for constant and decay release stages. As can been seen from experimental results (figure 4.2) and 2D results (figure 4.10 (i) to (iv)) starting from 20th day the urea front reaches the interface of granule and water environment. The release percentage rises rapidly and reaches to 89.65% at the end of 90th day.

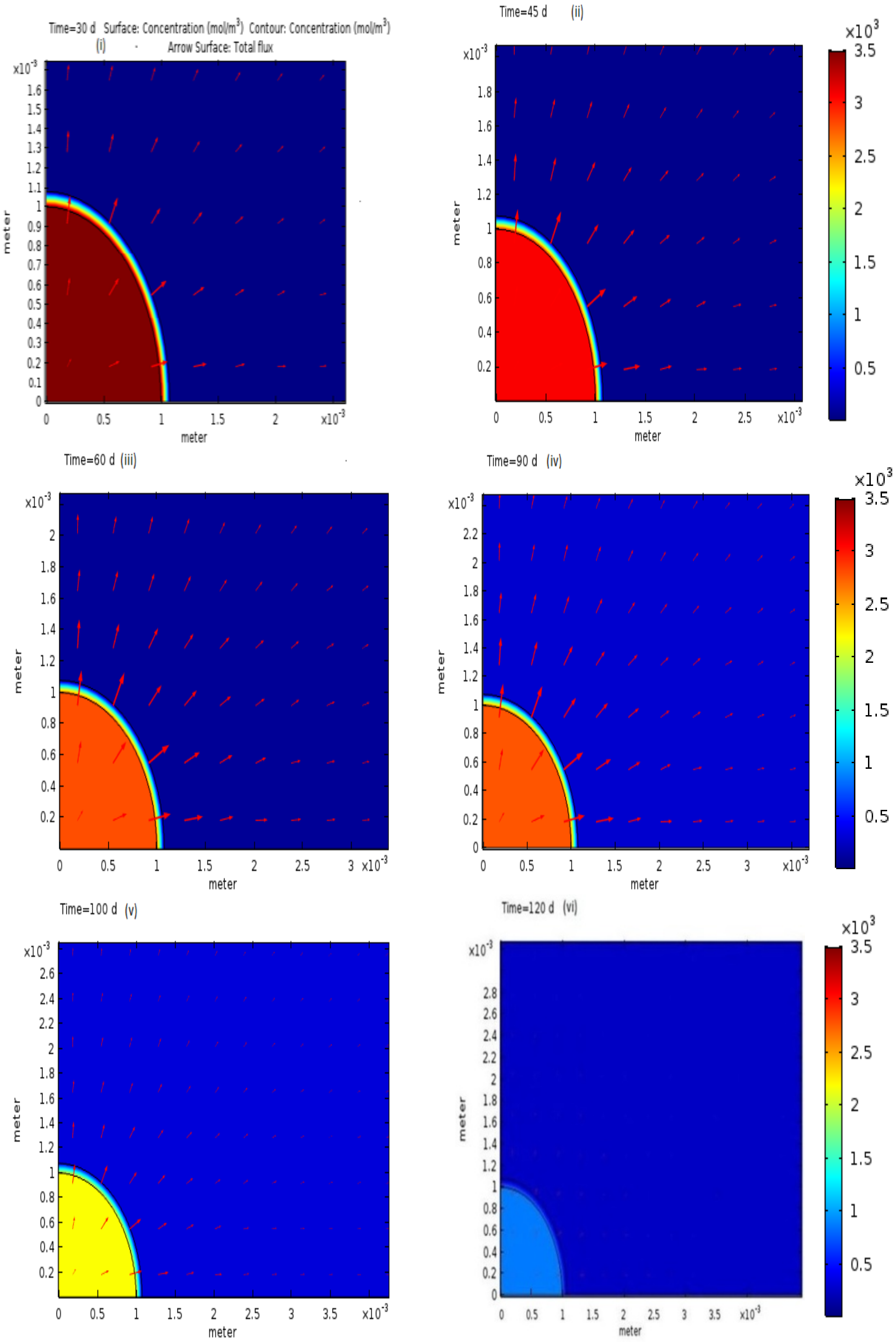


Figure 4.11. 2D release profile in NCU during constant (i to iv) and decay (v and vi) release phase. Colour legend represents urea concentration in range of 0-10500 mol/m³. Arrows represent diffusion flux which is related to nutrient release percentage

The colour change due to depletion of core and arrows depicting the release flux shows this 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.

Also as shown in figure 4.2 (experimental results) and 2D results in figure 4.11 (v and vi) the release becomes somewhat slower from 90th day to 120th day, and the amount of nitrogen release reaches 98.27%. 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.

CHAPTER 5

Modelling and Simulation of Nutrient Release from NCU with Imperfect Coating

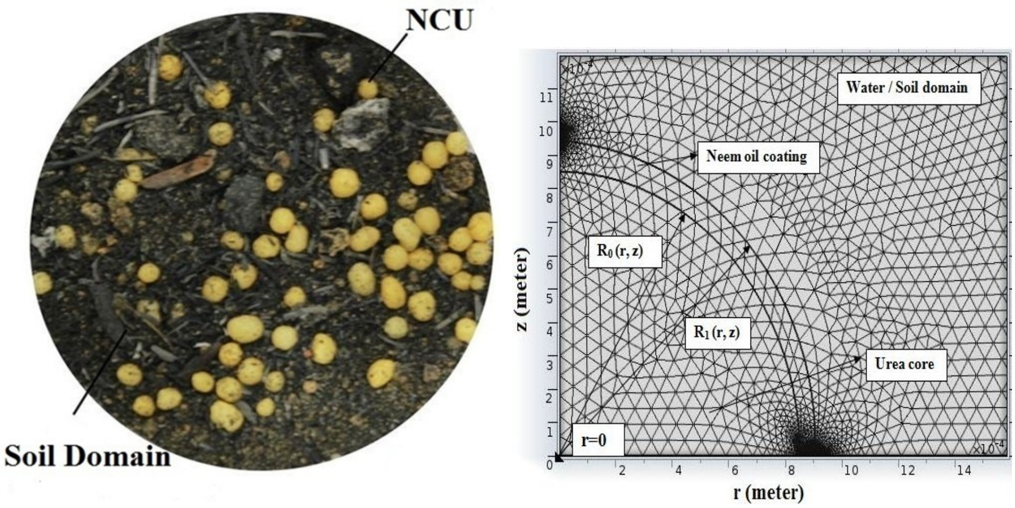
The accurate understandings of factors which influence the nutrient release from CRF and its uptake by plants along with appropriate methods to control the response mechanisms of materials in the soil environment are a prerequisite for selecting new material to improve nutrient uptake efficiency. So several field researches have been undertaken. Salman et al. [166] explained the release behavior of polyethylene-coated urea at different temperatures (25, 35, 45°C) in different media like water, sandy soil, and wetland rice soil. They found that coating quality was the main controlling parameter and presence of pinholes and imperfections in the coating resulted in higher release rates. Medina et al. [177] used an incubation soil column study to explore the release rates of CRF in different soil types and temperatures. They found that the nutrient release rate in soils increased as the textural class of soil changed from sandy to loamy. However, these studies lack in explaining release kinetics related to soil type and also did not presented any appropriate model to describe the same. This research gap can be attributed to the complex nature of soil texture and associated microbial activities. Also nutrient release in soil domain not only deals with the movement of nutrients within soil water but also within the soil matrix. To address this gap, Kochba et al. [178] proposed that the release of nitrate fertilizer into soil follows a first order kinetics and it is the water vapor penetration which is the controlling factor in the process. Gandeza et al. [164] used a quadratic regression model to demonstrate the affect of temperature on cumulative nutrient release from polyolefin-coated urea in the field. Brar et al. [179] analytically predicted the release of potassium (K) fertilizer by fitting experimental data obtained into several kinetic expressions such as zero order, first order, parabolic diffusion, and power laws as well as using Elovich equations. Xiaoyu et al. compared the nitrogen release data using the exponent and double-exponent equations representing Fickian diffusion and dissolving-eroding diffusion mechanism [180]. Most of the works focused on presenting regression models, whereas very few researchers presented the mathematical (mechanistic) modeling approach. Some workers like Jarrell and Boersma [181] combined diffusion through holes in SCU granules using a regression model to the percentage of open granules and presented a detailed computer program .They also incorporated the effects of microbial activity, temperature and soil water but did not include the effect of different soil types on nutrient release. Shavit et al. [172] presented the release of KNO_3 and urea using a tubular delivery device and coupled solute transport equations with the transport equation of vapor moisture within the device. However, they also failed to study the affect of soil environments have on nutrient release. Therefore developing a mathematical model that can reasonably predict the nutrient release behavior of CRF (using NCU) in soil environment can help in augmenting current research in the field. Also presence of coating imperfection is another important factor that has a important bearing on the nutrient release behavior [182].

In present chapter a model is proposed which couples the interfacial area ratio (IAR) equation with mass transport equation as explained in last chapter to explain diffusion transport of nutrient in porous medium (soil). The model takes into account the effect of coating layer imperfection and soil properties like porosity, surface area and particle size on nutrient release behaviour. The modelling and simulation of release from a single NCU granule with an imperfect coating thickness in water as well as soil domain is carried out. Experiments for nutrient release from NCU in water and soil environments are used for model validation. Also the model for imperfect coating is compared to the model for perfect coating (given in chapter 4) to show a better prediction of release behavior since actual coated urea particles seldom have perfect coating. Also the proposed model is used to investigate the effect of the coating variation and soil types on nutrient release from NCU.

The present chapter is divided into sections to present various aspects of mathematical modelling and related results for the case of imperfect neem oil coating on urea core. Section 5.1 presents the mathematical model development for nutrient release behaviour from a NCU granule in porous medium under given boundary conditions. Section 5.2 presents determination of diffusion in soil using IAR model. Section 5.3 discusses the inclusion of imperfections in coating thickness in the model. Section 5.4 presents different types of simulation studies carried out and their validation. Section 5.5 to 5.8 presents the results for four different simulation studies.

5.1 Development of mathematical model

NCU is placed in field is surrounded by a soil domain as shown in figure 5.1 (a). The NCU granule is assumed to be symmetrical across its horizontal and vertical axes (from the centre of the core) so for model development using a quarter of granule will suffice. The 2-D model for NCU with imperfect coating in soil/water environment is shown in figure 5.1 (b).



(a) (b)

Figure 5.1. (a) NCU as applied in soil. (b) Geometry and mesh generation of NCU granule (with core and coating layer) and its environment in 2D system, where $R_0(r, z)$ and $R_1(r, z)$ are radii of urea core and NCU granule, respectively

NCU on coming in contact with water or soil environments, gets wetted for a time period called lag time (t_0) (already explained earlier). After this the dissolved solid urea in core leads to nutrient diffusion through the coating into the surrounding environment. In this model, nutrient transport through coating layer can be described by mass transport equation for porous medium. The transient transport is governed by equation 4.1.

When the surrounding environment is soil, nutrient release in saturated porous medium is governed by equation 5.1 [107]

$$\varepsilon \frac{\partial C_k}{\partial t} + C_k \frac{\partial \varepsilon}{\partial t} + \nabla(C_k u) = \nabla[(\phi\ \tau_F\ D_{eff})\nabla C_k] + R_k + S_k \tag{5.1}$$

Here

C_k : concentration of species ‘k’ in the liquid (mole m^{-3}),

ϕ : liquid volume fraction,

D_{eff} : effective diffusivity ($m^2\ s^{-1}$),

τ_F : dimensionless tortuosity factor,

R_k : reaction rate expression that accounts for reactions in the liquid, solid, or gas phase,

S_k : arbitrary source term (fluid flow source or sink)

Since in present case the mass transfer of nutrient in the surrounding soil is diffusion governed phenomena so no source/sink or reaction takes palace. Thus equation 5.1 reduces to:

$$\varepsilon \frac{\partial C_k}{\partial t} + C_k \frac{\partial \varepsilon}{\partial t} + \nabla(C_k\ u) = \nabla[(\phi\ \tau_F\ D_{eff})\ \nabla C_k] \tag{5.2}$$

The above model is subjected to following assumptions:

(i) Nutrient release is governed only by means of diffusion, and no movement of soil water occurs within the domain i.e. stagnant condition prevails.

(ii) Constant temperature during release process

(iii) No reaction or loss of nutrient to the soil environment. However, this assumption is valid only under laboratory conditions where there is absence of leaching and the soil is sterilized prior to conducting the release experiments. This minimizes urease formation. However in actual field conditions, urea gets transformed to ammonium in the presence of urease.

In present work simulations of nutrient release in different soil types was carried out. The determination of diffusion coefficient in soil domain is explained below.

5.2 Diffusion coefficient in soil domain

The diffusion coefficient in soil domain (D_s) is slightly less than that in water domain because of the presence of the tortuous flow paths in soils. This difference is quantified by a dimensionless tortuosity factor (τ_F) [183]. Saripalli et al. [184] presented a model using the concept of interfacial area ratio (IAR) to determine the diffusivity of a solute in soil (D_s) knowing the diffusivity of same solute in water (D_w). The tortuosity factor in soil incorporated in the present model based on interfacial areas ratio (IAR) is calculated as follows:

$$\tau_F = \frac{3.3\varepsilon}{Sr_p} \tag{5.3}$$

Here

S : specific surface of porous (soil) medium ($m^2\ m^{-3}$),

r_p : particle radius of the porous (soil) medium (m),

ε : porosity,

τ_F : dimensionless tortuosity factor

Also the diffusion of urea in water (D_w) is concentration dependent and can be determined by using equation 4.3.

5.3 Incorporation of coating thickness variation in present model

Almost all existing models are based on the assumption that CRF granules have a perfect coating and are of spherical shape. But in actual use, they are neither spherical nor have a perfectly uniform coatings. However, as explained in chapter 4, the coating thickness is a vital parameter in determination of actual nutrient Release.

In development of present model although the urea particle is assumed to be spherical but the neem oil coating is taken to be non uniform. This non uniformity is a result of coating process being adopted. The imperfection in coating thickness is shown in figure 3.6 (SEM images). The normal distribution as given by equation 5.4 and depicted in figure 5.2 can be used to approximate the variability in coating thickness:

$$f(x, \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \qquad (5.4)$$

Here

$f(x, \mu, \sigma)$: probability density function,

μ : average of coating thickness distribution,

σ : standard deviation of coating thickness distribution

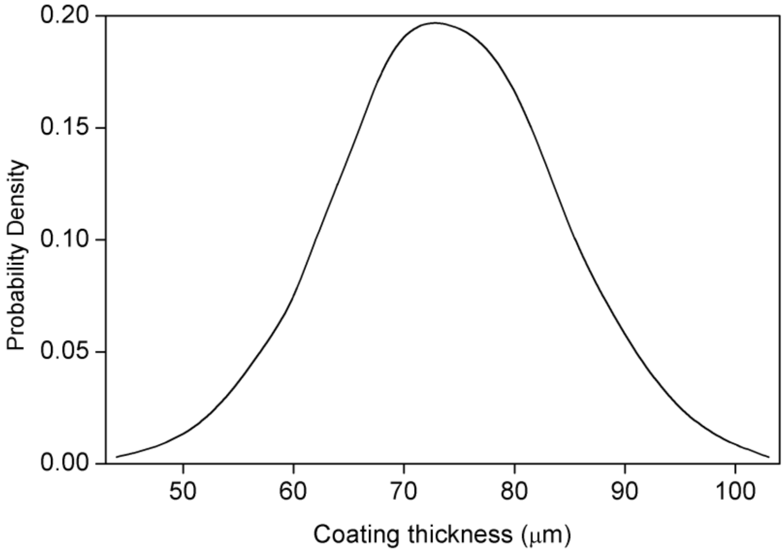


Figure 5.2. Coating thickness (average coating thickness 72μm) distribution in NCU represented by normal distribution

To implement concept of imperfect coating on a urea granule we utilize the concept of cumulative density function (*l*_distribution) as given in equation 5.5, which is a function of parameter (s) representing minimum to maximum coating thickness

$$l\_\text{distribution}(x) = \frac{1}{2}\left[1 + \text{erf}\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right] \qquad (5.5)$$

When s varies from minimum to maximum coating thickness (38 μm to 120 μm) *l*_distribution varies from zero to one and θ varies from 0 to π/2 with formula below

$$\theta = \frac{\pi}{2} * l\_\text{distribution} \qquad (5.6)$$

The parametric equations which were used in COMSOL to plot imperfect geometry on core of urea particle in a quadrant are given by equation 5.7-5.8.

$$\mathrm{r} = (s + \mathrm{R}_0) * \cos\left[\frac{\pi}{2} * l\_\mathrm{distribution}(s)\right] \tag{5.7}$$

$$z = (s + R_0) * \sin\left[\frac{\pi}{2} * l\_\mathrm{distribution}(s)\right] \tag{5.8}$$

Using these equations we get figure 5.3

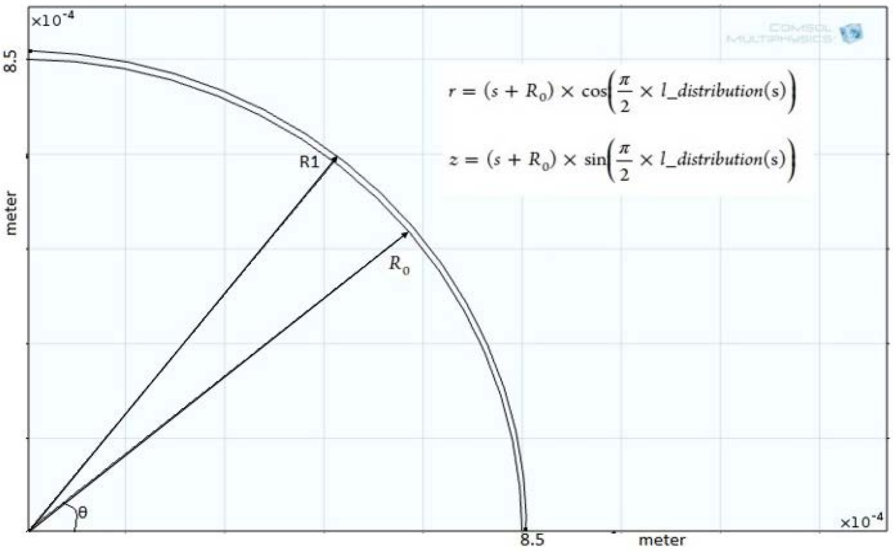


Figure 5.3. Quadrant of urea granule in 2D geometry where core radius (R_0) is 0.85mm and R_1 is variable outer radius, which is determined by parametric equations

Statistical distribution of coating thickness is obtained using the standard deviation of coating thickness (σ) which is used to investigate the effect of variations in coating thickness. During simulation runs granules of the same average thickness (72 μm) but with varying distributions and standard deviations (σ) of 1, 5, and 10 μm were used.

The effect of imperfections in coating thickness is shown in figure 5.4. It can be seen that where the coating is thinner, resistance is lower and hence it permits easier nutrient transport outward. To have clear picture of curves above, curves are zoomed and results are shown in figure 5.5.

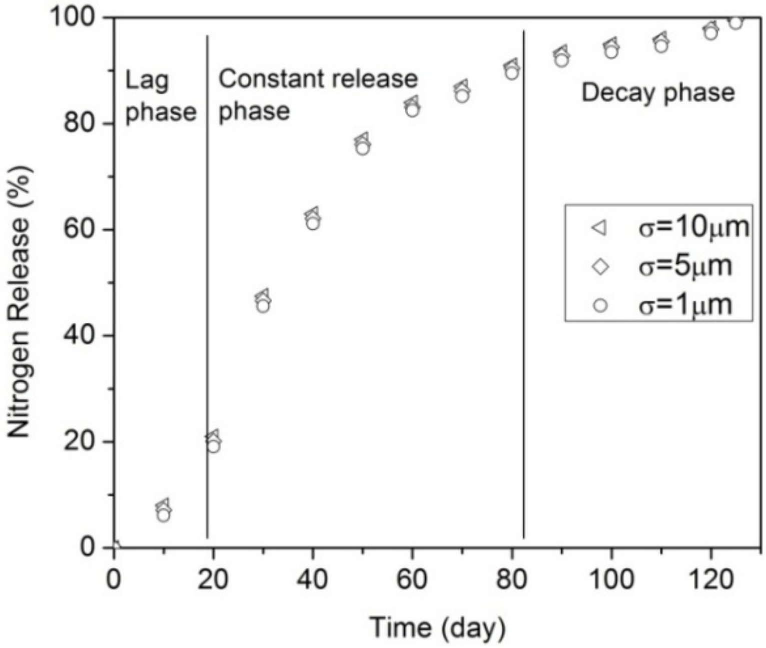


Figure 5.4. Comparison of nutrient release profiles for NCU granules with different distribution (σ=10, 5, 1). The granules have the same average coating thickness (72µm)

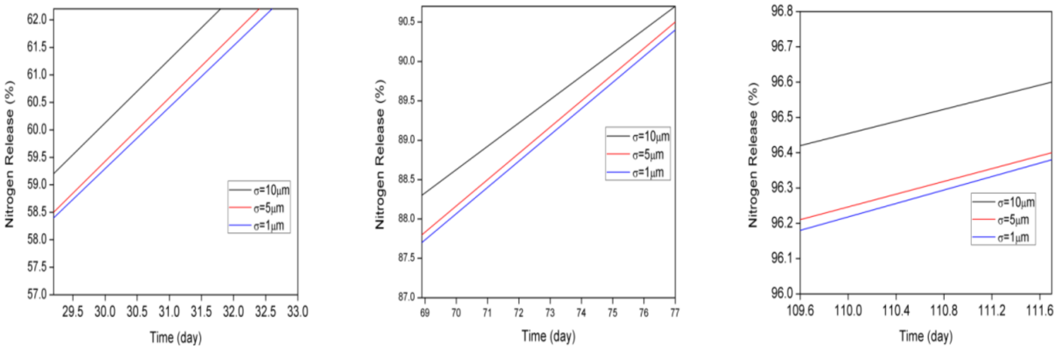


Figure 5.5. Zoomed graph for (L-R) at (i) 29 to 33 (ii) 69 to 77 and (iii) 109 to 112 days

From 2D simulation results for the present case of imperfect neem oil coating on a single granule, the nutrient diffusion rate through the thinner part of the coating is higher than other parts. As can be seen from figure 5.6 higher nitrogen flux movement takes place toward the thinner coating zone and the trend is intact until the end of the release phenomena. Hence, the nutrient release to the environment is higher and faster even at the final stage of the release process in contrast to the perfect coated NCU granule. In other words, the presence of coating imperfection in a single NCU granule leads to an enhanced nutrient release rate as compared to that from a perfectly coated one.

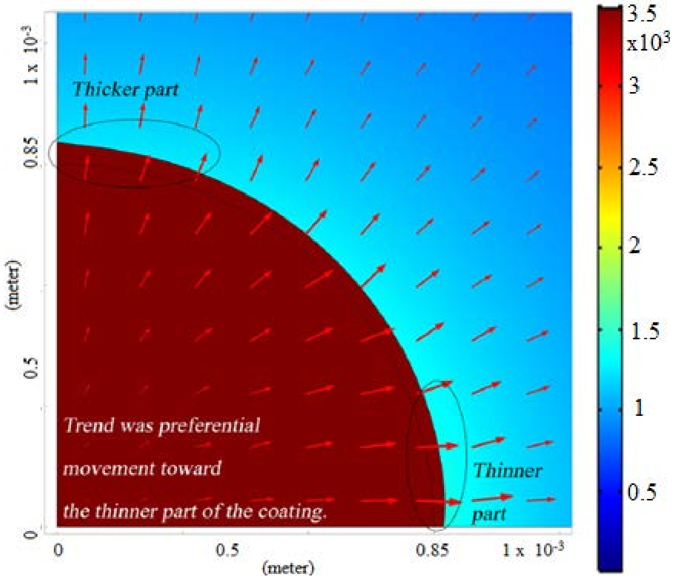


Figure 5.6. 2D results for nutrient release from a imperfectly coated NCU granule. Color legend represents urea concentration (mol m^{-3}), and arrows give the diffusive flux of nutrient. The length of arrow depicts the quantity of diffusive flux

5.4 Model simulation and its validation

Present model developed using equation 4.1, 4.3, 5.2 and 5.3 is implemented using 2D symmetrical coordinates. The coating layer imperfection throws in the additional complexity. Thus, finite element method (FEM) using backward differencing scheme was used to predict the nutrient release from NCU under the given geometric irregularity and complex set of equations. The mesh generation leads to creation of approximately 40,456 elements of average quality of 0.985. Error tolerance was set between 10^{-19} to 10^{-16} during the calculation process and the accuracy of simulation using mesh convergence analysis was 0.00125%. Maximum time step used in simulation is 1 day.

The release is a staged process as explained earlier so simulation comprised of two stages namely constant and decay release. Thus initial and boundary conditions used in the model are stage dependent and given in table 4.1.

The total amount of nitrogen/nutrient release at any time t is calculated as

$$\text{Release } (\%) = \frac{M_{\text{Release }}(t)}{M_{\text{Total Urea}}} \times 100\% \qquad (5.9)$$

Here

Release (%) : wt % of nutrient released from CRF at any time t,

$M_{\text{Release}}(t)$: cumulative nutrient/urea released from CRF at time t,

$M_{\text{Total Urea}}$: total urea present in CRF at the beginning

In order to validate the model four different types of simulation runs were carried out:

(1) In **first simulation** water is taken as surrounding environment. For this case, $\epsilon = 1$ and $\tau_F = 1$. The results were compared with the experimental data generated in section 3.3.1 using UV−Vis spectrometer. The parameters were used to simulate and validate nutrient release in water are given below in table 5.1.

Table 5.1. NCU parameters used in simulation study to obtain and validate nutrient release in water

Simulation parameter	**Value**
Core radius (R_0), mm	0.85
Mean of coating thickness (μ), μm	72
Coating standard deviation (σ), μm	1
Lag time (t_0), day	19
Effective diffusivity (D_{eff}), $m^2\,s^{-1}$	3.0×10^{-14}

(2) The **second simulation** was conducted for the nutrient release from NCU in sandy clay loam soil. The results were compared with the experimental data generated in section 3.5 using weight loss method. The parameters for NCU used in this simulation are same as those given in table 5.1 whereas soil parameters are given in table 5.2.

Table 5.2. Soil properties used in model to obtain the nutrient release from NCU in soil domain[185]

Simulation parameter	**Value**
Porosity (ε), %	42
Specific surface area (S), $m^2\,m^{-3}$	450
Particle radius (r_p), μm	100

(3) In **third simulation** nutrient release in water and soil environment were compared.

(4) In **fourth simulation** nutrient release in different soil types is carried out to see its (soil type) effect on nutrient release behavior. The soil properties were obtained from the literature and are given in table 5.3. The mass transport within the soil environment is calculated using equations 4.3, 5.2 and 5.3.

Table 5.3. Soil properties used in model to study the effect of soil types [185]

Soil type	**Porosity (%)**	**Particle density (kg × m^{-3})**	**Particle size (cm)**	**Surface area (cm^2 × g^{-1})**
Sand	32	2,720	0.1	30
Silt	45	2,327	0.001	125,000
Clay	50	2,440	0.0002	2,000,000
Silt loam*	50	2,439	0.00092	262,771

*Silt loam composition: 9.27% clay, 61.89% silt and 28.84% sand

5.5 Results for first simulation

As mentioned above the first set of simulation studies correspond to the determination of nutrient release from imperfectly coated NCU in surrounding water domain. The results for present model is compared with (a) the model presented in chapter 3 in which coating imperfections were neglected and (b) with the experimental result for nutrient release presented in section 3.3.1.

Figure 5.7 shows the result for this comparison. It can be inferred from the result that porous model corresponds more accurately with the experimental findings. The SEE for porous model and multi-diffusion model (with perfect coating) was found to be 0.02 and 0.03 respectively. The closeness of porous model with experimental results is due to the inclusion of coating imperfections in the model since actual CRF also have imperfect coating.

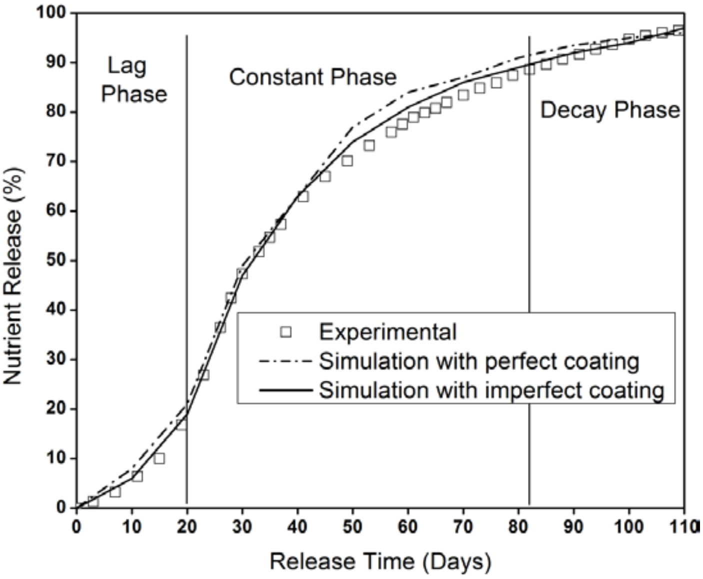


Figure 5.7. Comparison between the present model, model with perfect coating and experimental data on nutrient release profile of NCU in water

5.6 Results for second simulation

The second set of simulation studies focused on unveiling the nutrient release from NCU in soil domain. The diffusivity in the soil domain was calculated using IAR formula as explained above. Simulation results were compared with weight loss method studies carried out to determine nutrient release in sandy clay loam soil as explained in section 3.5. The results are presented in figure 5.8.

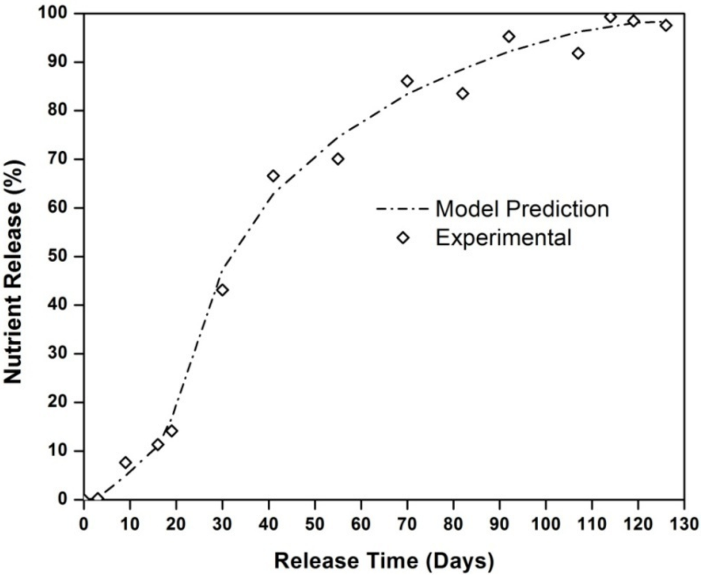


Figure 5.8. Comparison between simulation and experimental results of nutrient release from NCU in soil

The simulation results in soil domain corresponded fairly well with experimental results and the SEE value was found to be around 0.09. The minor deviations in simulation results from experimental ones may be due to factors like mismatch in actual soil properties and those chosen in simulation as parameter. Also some error may be due to the weight loss method used in experimentation.

5.7 Results for third simulation

The first two simulation studies have established that porous model accurately predicts the nutrient release behavior of NCU, so in third simulation results are compared for nutrient release in sand (soil) and water environments (figure 5.9). The nutrient release in soil is retarded as compared to that in water thus establishing the fact that environmental properties have a bearing on the release rate. However the difference in nutrient release in sand and water is not very large. This in indicative of the fact that irrespective of the surrounding domain the main controlling factor for nutrient release is the coating/barrier layer on the urea core.

At the end of the constant release phase the divergence in release rate in soil and water domain become more pronounced due to the fact that the controlling factor slowly changed from coating layer to surrounding environment since there is low concentration gradient in the environment domain at this stage. So the driving force within the environment became smaller than that in the coating layer and thus it began dominating the release process and this domination is more evident in case of soil than water. The above observations are helpful in development of new CRCU products since experimentation in water domain adequately mimic the nutrient release pattern of CRF in soil.

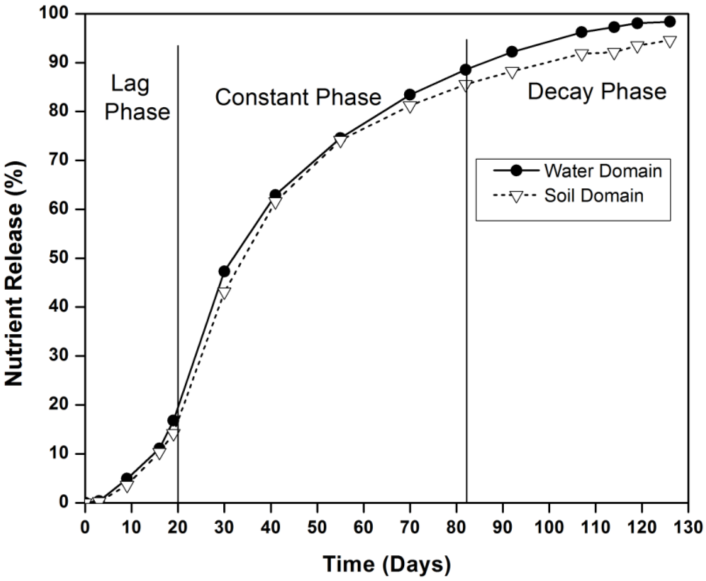


Figure 5.9. Comparison of nutrient release for NCU in water and soil domain using model results

5.8 Results for fourth simulation

The simulation results for the nitrogen release from different soils types namely sand, silt, silt loam and clay are shown in figure 5.10. From figure it can be seen that from 0 to 20 days, the nutrient releases behavior in different soils is overlapping since this corresponds to lag phase in which external environment plays a passive role.

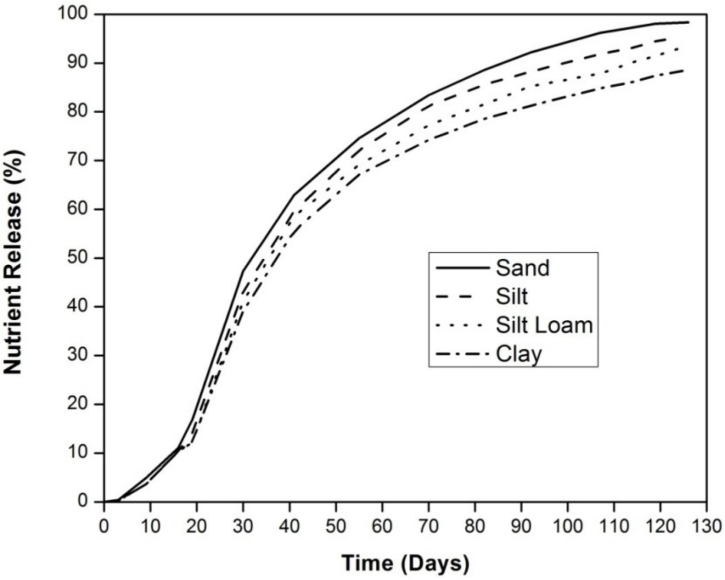


Figure 5.10. Comparison of nutrient release in NCU in different types of soil domain using porous model results

However, nutrient release from NCU in release to sand, silt, silt loam, and clay increased from 47.34%, 43.13%, 41.05%, and 38.37% after 30 days to 83.41%, 81.25%, 77.18%, and 74.47% after 70 days, respectively. The difference between nutrient release in soils also increased as time progresses and the maximum difference is 11.62% at 92 days between the release in clay and in sand.

Although, the differences in release percent are small, it can be affirmatively said that soil type has a direct bearing on nutrient release behavior and the release rate decreases as the soil environment changed from sand to clay. The release pattern of clay soil is quite different and gives lower release percentage at any time since it has a significantly high specific area (table 5.3) leading to a higher tortuosity whereby presenting a resistance to nutrient diffusion. Thus the present model obtained by incorporating IAR formula in nutrient mass transport equation in porous medium helped in predicting nutrient release in various soil types whose properties can be obtained either from literature or experiment. Although as pointed in above section since nutrient release pattern in soil is quite similar to that in water. Therefore when studying any new CRF the release pattern in water can be used as a reference for comparison because conducting experiments in water domain are easier and consistent than in soil domain.

In above simulations, it is shown that the release profile from single NCU granule is similar in water and soil; however the nutrient distribution in these environments will differ since water domain present lower resistance then soil thus allowing easy nutrient movement outward. But this should be studied separately since in actual practice the concentration in surrounding environment is a major deciding factor for estimating the loss of nutrient through reaction and leaching of nutrients and also for nutrient uptake by plant roots. Also additional complexity in determining the nutrient concentration in surrounding environment is added due to presence of population of granules.

Figure 5.11 present the 2D results for nitrogen distributions in different soil type to show that the nutrient distribution is affected by the soil type. In the vicinity of the NCU granule the nitrogen concentrations were found to be 60, 140, 210 and

270 mol × m^{-3} for sand, silt, silt loam, and clay, respectively at 20th day. The concentration was markedly higher for silt loam and clay soils as compared to that for sand and silt. Since even for a small clay content presence in soil the specific surface area increases enormously this leads to a mass transfer resistance in the soil domain and thus builds up a higher nitrogen concentration in the surrounding of the NCU granule compared to silt or other soil type. Also in actual field conditions, the nutrient concentration distribution are influenced by other factors like water retention capacity of soil and irrigation condition, these are not taken into consideration for in present model. A build up of concentration can translate into higher N loss through NH_3 volatilization which is accelerated by high soil pH. Also soil acidity can increase due to nitrification [186,187]. Thus, for soil domain in general and for clayey soil in particular nitrogen build up can have a detrimental effect on soil microbes and young roots if NCU is applied too near to the plant roots. On the other hand the mass transfer resistance posed by the soil environment hampers the nutrient uptake by plant root if NCU or any CRCU is applied too far from the root. Since nutrient release behaviour varies for different CRF and a variation in soil types also presents a different nutrient release behaviors and concentration distributions, an accurate knowledge of nitrogen distribution data is of utmost importance for fertilizer management in terms of nutrient uptake or loss during fertilizer application in soil.

Thus, the proposed porous model incorporating the effect of coating imperfections can be effectively used to study the nutrient release behaviour from NCU in water and also in soil domain under saturated and stagnant conditions. The coating characteristics can be determined by experiments and soil properties can be obtained either from literature or experiments which are used as input to predict nutrient release in soil. Thus it can be concluded that the model utilizes nutrient release from NCU in water to study its release in various soil domains. However further refinement of model is required for including effects of unsaturated soils microbial activities and irrigation conditions.

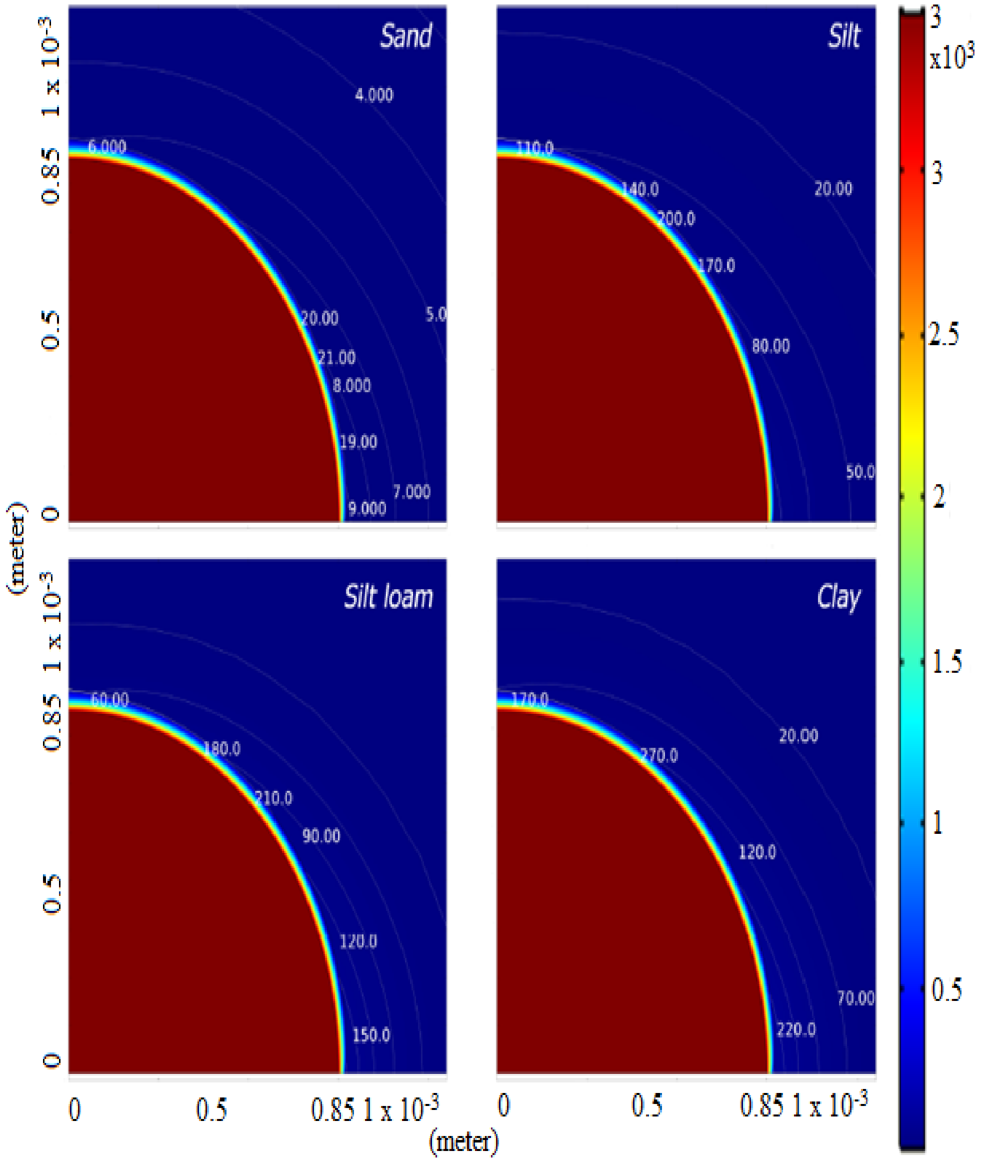


Figure 5.11. Comparison of nitrogen concentration distribution in vicinity of NCU granule different soil domains after 20 days

CHAPTER 6

Conclusions and Recommendations for Future Studies

The present thesis is an attempt to provide a scientific and systematic analysis of NCU through experimental and mathematical analysis of its physicochemical properties and release dynamics. NCU is a novel CRF and its use in agriculture is an example of green technology that not only reduces nitrogen loss caused by volatilization and leaching, but also alters the kinetics of nutrient release, which, in turn, provides nutrients to plants at a pace that is more compatible with their metabolic needs. Since as per Government of India policy, 100% of indigenously produced and imported urea is being neem coated w.e.f 1st September, 2015 and 1stDecember, 2015 respectively so a comprehesive study is needed to understand various scientific aspects of the same.Present work is first of its kind to do so for NCU, since all previous studies on NCU were limited to explianing its effect on various crops and also no inhouse R&D was carried out and published by fertlizer companies who are mearly producing the NCU as per a fixed receipe.

6.1 Conclusions

The major conclusions that can be drawn from the present work are:

1. Among the available techniques fluidized bed coating process being experimentally simple to design and operate for forming small coated particles holds promise for making NCU of reasonable quality. Also the NCU particles produced using fluidized bed shows same property as those of commercially produced NCU manufactured using drum or spray coaters. Around 1 liter neem oil can satisfactorily coat about 100 kg urea.
2. Using particle size distribution analysis it was found that NCU maximum particles are available in diameter range of 1.7 mm and 2.0 mm. Particle strength also increases due to coating (reduction in particle breakage after neem oil coating) since less number of particles of NCU are present in lower size distribution ranges.
3. NCU contains 43.79% of nitrogen as compared to 46.44 % in UCU. The EDX also shows a lower peak of nitrogen in case of NCU which suggests

that about 3 % reduction in total N was observed for NCU as compared to UCU. It is due to inherent nature of the coating process, in which the urea granule undergoes, spraying, wetting and drying process which may cause some loss of nitrogen.

4. Due to coating NCU shows low dustiness.
5. The dissolution rate in water is slower for NCU as compared to UCU and dissolution rate increases with temperature.
6. NCU has higher crushing strength as compared to some other commonly used CRF like PCU and BCU indicating its better performance as CRF due to improved strength.
7. SEM study shows that although coating is imperfect but coating imparts more homogeneity to the urea surface and since neem oil coating is dense, no visible sign of gaps or cavities in coating layer were observed.
8. The FTIR spectra study of UCU and NCU show no significant variation in peaks indicating that there is no chemical interaction between the urea and the coating material. Also in XRD results since no new peaks in the spectra of NCU are observed, it may be inferred that no new phases are formed during the coating process. So it may be concluded that the interactions between the Neem oil and Urea are basically physical and not chemical in nature.
9. The nutrient release profile from NCU determined experimentally in water and soil domain shows a sigmoidal shape, follows the diffusion stages as described in literature and satisfies the CEN criteria for CRF. Moreover a single application of NCU in field can match the nutrient requirement of most of the crops which have a maturity period of around 100-120 days and NCU is also active for same duration. Thus NCU acts as a perfect CRF along with other advantages as mentioned in earlier chapters.
10. A rapid technique is presented to estimate the nutrient release percentage at 25˚C can be conveniently and accurately predicted by utilizing the rate 100˚C.Unlike the earlier available methods of prediction of nutrient release from CRF products, the rapid method described in present study is reproducible and does not use or require chemicals for analysis. Therefore,

the proposed methodology can be easily applied both by the fertilizer manufacturers and distributors for accurate estimation of CRF release rate and duration.

11. The comparison of release rate for water domain obtained from spectrometry method and for soil domain using weight method shows that the release in sand (soil domain) was slower than in water, clearly indicating that environmental properties contribute to the restriction of nitrogen release. However, the difference of release in sand and water is not very large. This shows that the main controlling factor for nitrogen release is the coating layer itself and not the external environment that surrounds the coated fertilizer, be it water or sand. Therefore when studying any new CRF the release pattern in water can be used a reference for comparison because conducting experiments in water domain are easier and consistent than in soil domain.
12. A multi diffusion model is developed to predict nutrient release from NCU assuming perfect coating. Model is developed for multilayer including the Neem Oil coating, water domain and it couples the finite element approximation with 2D geometry, also to improve the accuracy of simulation urea diffusivity in water is taken as a function of its concentration. 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/soil environment. To establish the reliability and robustness of the model, a comparison was carried out between the model results and corresponding experimental data obtained from literature for other CRCU. The simulation result for nutrient release from single NCU granule corresponded well with our experimental data and literature data. The standard error of estimate (SEE) used to determine the accuracy between simulation and experimental 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 that cited in the literature.

13. The modelling studies revels that core radius and coating thickness have an antagonistic effect on nutrient release rate from NCU. So, in order to increase the release time an increase in core radius is a convenient and effective option as compared to manipulating the coating thickness.
14. The regression analysis of data yields a linear relationship which can be mathematically expressed as:

$$Release\ rate = \left(-0.079 + 0.0357\left(\frac{{R_0}^2}{a}\right)\right) 10^{-10}\,\frac{mol}{s}$$

The above relation is in tune with the diffusion theory of mass transport processes. The relationship shows that release rate varies inversely with the coating thickness and varies directly with the square of core radius. Since diffusive flux is inversely related to coating thickness so release rate also varies inversely with the same. Also the release rate depends on the available surface area for diffusion to take place, which is nothing but equivalent to square of core radius R_0. Thus above provides a better estimate to determine the cumulative effect of core radius and coating thickness on nutrient release rate from NCU in particular and for other CRCU in general during constant release stage.

15. Another model is proposed which couples the interfacial area ratio (IAR) equation with mass transport equation to explain diffusion transport of nutrient in porous medium (soil). The model takes into account the effect of coating layer imperfection and soil properties like porosity, surface area and particle size on nutrient release behaviour. The modelling and simulation of release from a single NCU granule with an imperfect coating thickness in water as well as soil domain is carried out. Experiments for nutrient release from NCU in water and soil environments are used for model validation. Also the model for imperfect coating is compared to the model for perfect coating. The porous model show a better prediction of release behavior since actual coated urea particles seldom have perfect coating. Also the proposed model explained the effect of the coating variation and soil types on nutrient

release from NCU. Model predicted that places where the coating is thinner, resistance is lower and hence it permits easier nutrient transport outward which is also seen in actual practice.

16. The porous model showed that at the end of the constant release phase the divergence in release rate in soil and water domain become more pronounced due to the fact that the controlling factor slowly changed from coating layer to surrounding environment since there is low concentration gradient in the environment domain at this stage. So the driving force within the environment became smaller than that in the coating layer and thus it began dominating the release process and this domination is more evident in case of soil than water. The above observations are helpful in development of new CRCU products since experimentation in water domain adequately mimic the nutrient release pattern of CRF in soil.
17. Simulation results showed that soil type has a direct bearing on nutrient release behaviour and the release rate decreases as the soil environment changed from sand to clay. The release pattern of clay soil is quite different and gives lower release percentage at any time since it has a significantly high specific area leading to a higher tortuosity whereby presenting a resistance to nutrient diffusion.

6.2 Recommendations for future studies

Based on the conclusions in the previous section, several areas of improvement have been identified for future works which are as follows:

1. The model developed above could accurately predict the release rates but does not gives actual spatial distribution of nutrient in soil which is a interplay of several other factors like water retention capacity of soil, and irrigation condition, microbial activities non homogeneity of soil particle size. A more robust model taking above factors into consideration can be developed.
2. In order to improve the accuracy and reduce the small mismatch between the experimental and simulation results, variations in particle shape and presence of surrounding particles should be studied.

3. The modelling of nutrient release from a population of particles is recommended to closely support the experimental observations.
4. Although it is shown through experimental and modeling results that the release profile from single NCU granule is similar in water and soil; however the nutrient distribution in these environments will differ since water domain present lower resistance then soil thus allowing easy nutrient movement outward. This should be explored and incorporated in future works since in actual practice the concentration in surrounding environment is a major deciding factor for estimating the loss of nutrient through reaction and leaching of nutrients, and also for nutrient uptake by plant roots.
5. The COMSOL results may be verified using some other CFD tool.

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  Indian Institute of Technology, Kharagpur, (INDIA)
- July 2010-Dec 2010 : Assistant Professor in Chemical Engineering
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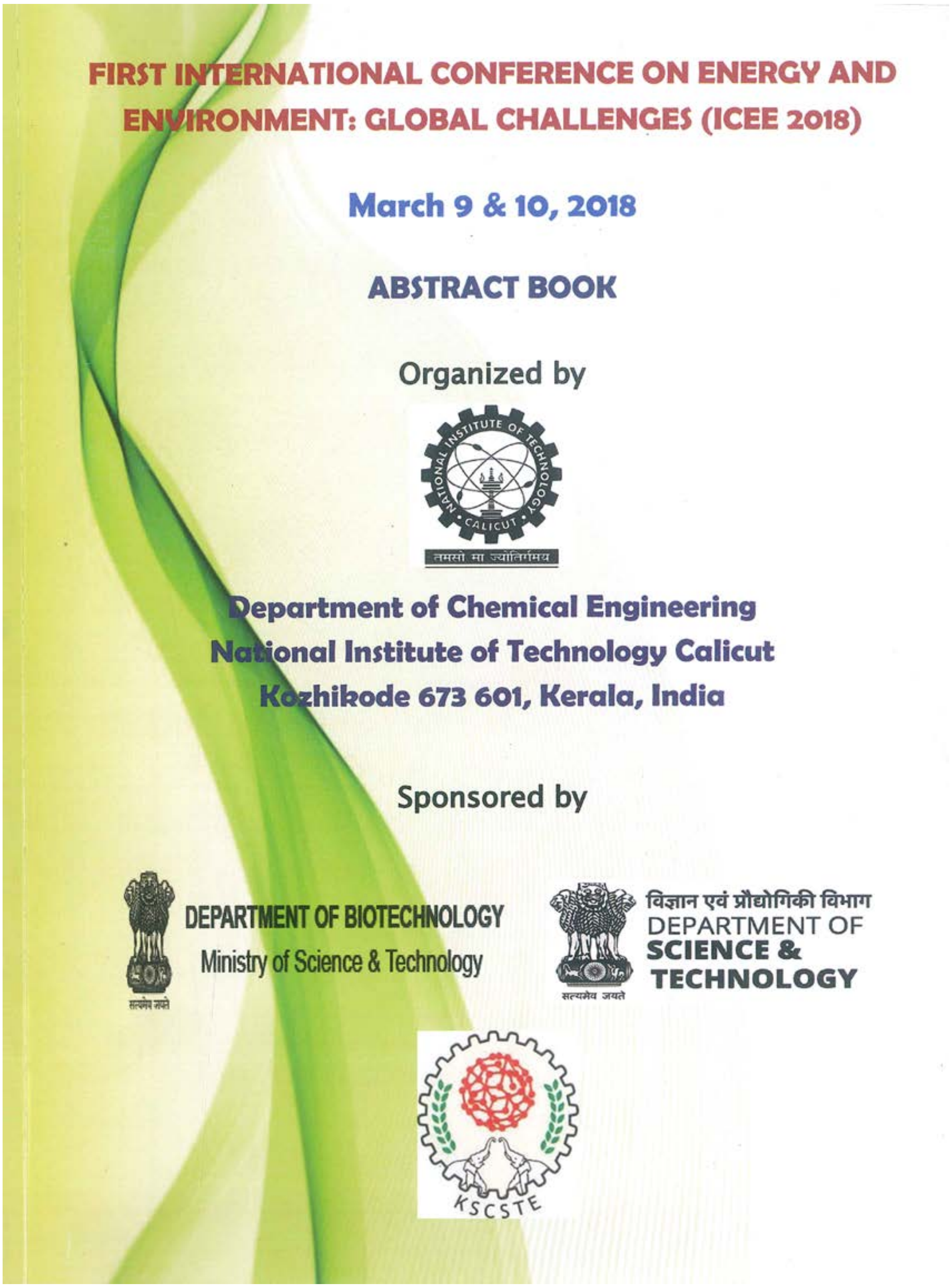
LIST OF PUBLICATIONS (from present work)

Conferences: **(04)**

1. **Shiv Om Meena** ,Manish Vashishtha and Ankush Meena,*"* Development of a Rapid Method for Determination of Nitrogen Release from Coated urea fertilizer", *International Conference on Energy and Environment: Global Challenges* (ICEE2018), Department of Chemical Engineering, National Institute of Technology Calicut, Kozhikode, Kerala, India, March 8-9, 2018. **(Presented and Published in Proceedings)**
2. **Shiv Om Meena**, Manish Vashishtha and Ankush Meena, "Modelling and Simulation of Nutrient Release from Neem (Azadirachta Indica) Oil Coated Urea", *International Conference on Environmental Science and* Technology (ICEST-2018), Prague, Czech Republic, June 22-24, 2018. **(Presented and Published in Proceedings)**
3. **Shiv Om Meena** and Manish Vashishtha, "Determination of Nutrient Release from Neem Oil Coated Ureain Soil Domain Using Weight Loss Method", *Seamless Chemical Engineering in Service of Humanity: Innovations, Opportunities & Challenges* (CHEMCON–2018), December 27-30, 2018, NIT Jalandhar (Punjab). **(Presented)**
4. **Shiv Om Meena**, "Controlled Release and Slow Release Fertilizers as Nutrient Management", *International Conference on Global Trends & Future Prospects in Multidisciolinary Research,* February 04-07, 2019, NIT Jalandhar (Punjab). **(Presented)**

Journals: **(02)**

1. **Shiv Om Meena**, Dr. Manish Vashishtha and Ankush Meena ; (2018) Experimental Determination of Nutrient release from Neem Oil (Azadirachta indica) coated urea, *Chemical Methodologies*, Vol. 2, 300-308, 2018.
2. **Shiv Om Meena**, Manish Vashishtha and Ankush Meena ; (2018); Modelling and Simulation of Nutrient Release of from Neem (Azadirachta indica) Oil Coated Urea, *Journal of Advanced Agricultural Technologies*. (**Accepted)**



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ABSTRACT BOOK

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KSCSTE

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Abstract

Biofuels are one of the promising alternatives for petroleum-based fuels. Biofuels produced from agricultural residues are viable and of current trend in research. In this context, this work has been by utilising the waste potatoes from potato go-downs. Potato starch produced from waste potatoes was used as an economical source for biomass and bioethanol production by Saccharomyces cerevisiae. At first, potato starch is produced via autoclaving. Sulphuric acid (1%) acid hydrolysis of potato starch was carried out for 1h and amylase enzyme was used for enzymatic hydrolysis. S. cerevisiae was utilized to ferment the acid-treated and enzyme treated potato starch under aerobic conditions. The process conditions such as temperature, initial yeast concentration, and substrate concentration are optimized using Box-Behnken RSM design. At the optimal process condition the maximum yield of ethanol was found to be 26.51 g/L for acid hydrolysis root and 25.89 g/L for enzymatic hydrolysis root.

Keywords: Bioethanol, Potato Waste, Box-Behnken, Enzyme Hydrolysis, Acidic Hydrolysis, Optimization

Abstract Code: ICEE150/ ORAL

Development of a Rapid Method for Determination of Nitrogen Release from Coated Urea Fertilizer

Shiv Meena, Dr. Manish Vashishtha* ,Ankush Meena
Malaviya National Institute of Technology, Jaipur, India
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Abstract

Controlled release fertilizers (CRF) are manufactured to provide nutrient release over different durations and rates to match the requirement of different crops over wide ranges of nutrient requirements. Since release from CRF span over many days, so a rapid technique is needed to verify the label specifications of nutrient release rate and duration. In present study Polymer-coated urea (PCU) and Neem coated urea (NCU) (both have 46% Nitrogen) fertilizer were used. The nutrient release test of PCU at 25°C showed that 47.95% of total N was released over 126 days (d) and at 100°C in water 100% of N release occurred in about 165 hours (h). Similarly release test for NCU at 25°C showed that 98.35% of total N was released over 126 days (d) and at 100°C in water 100% of N release occurred in about 245 hours (h). Regression equations were developed for cumulative nutrient release as a function of release time separately at 25°C and 100°C. Using the above regressions, the release duration for a given percent nutrient release at each temperature was calculated. These values were then used to establish a relationship between the release duration at 25°C as a function of that at 100°C. This study demonstrated that a rapid nutrient release test at 100°C successfully predicted nutrient release rate and duration at 25°C, for both PCU and NCU. The developed relationship is also useful to predict the Nutrient release duration at 25°C of an unknown CRF product by conducting a rapid release test in water at 100°C. Therefore, this rapid test can be employed to find the release rate and time of many other CRF.

Keywords: Controlled Release Fertilizer, Polymer Coated Urea, Neem Coated Urea

2018 HKCBEES PRAGUE CONFERENCE ABSTRACT

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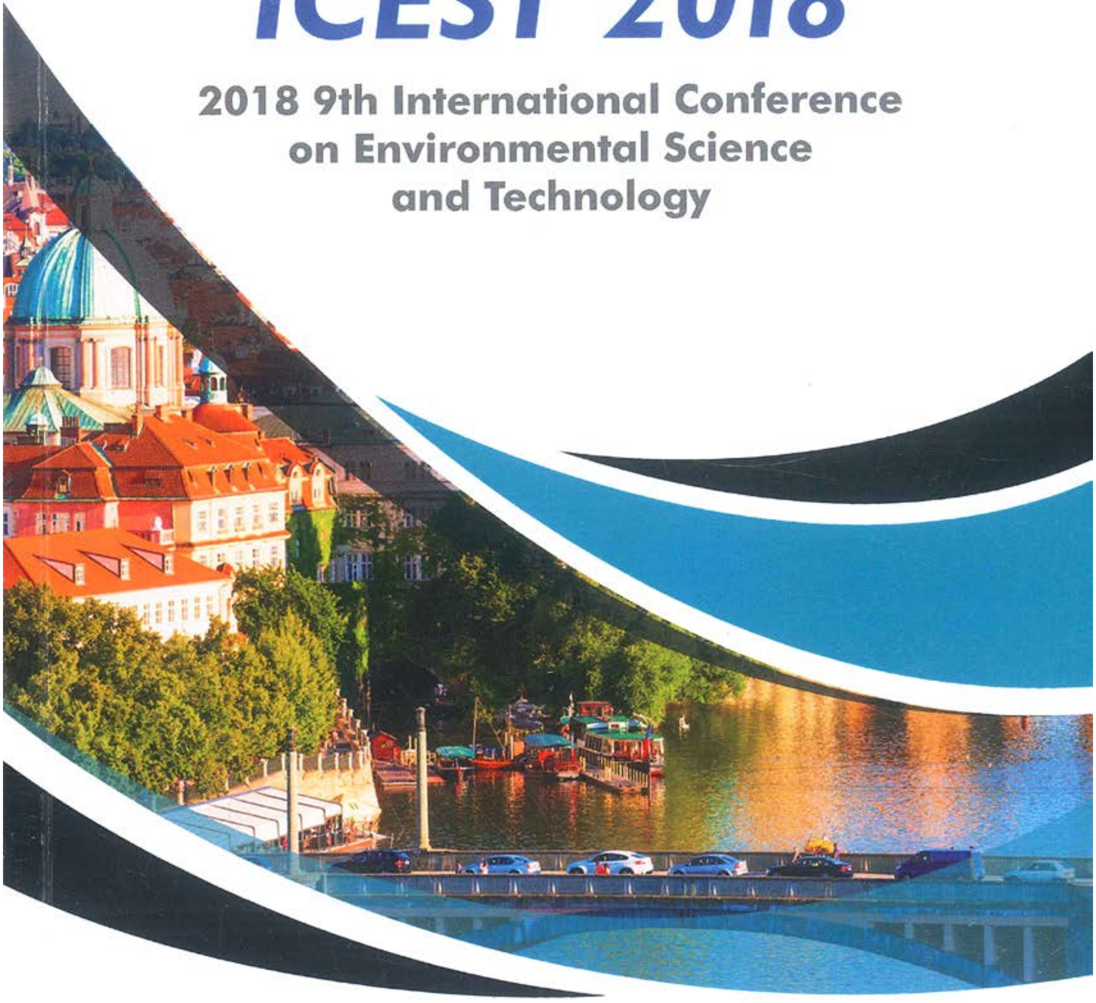

June 20-22, 2018
Prague, Czech Republic

the main cause of this irreversibility is heat transfer with the high-temperature difference. To improve this, we should increase heat exchange and then reduce the temperature difference. For the system performance improvement, particular attention should be paid to this part to reduce the outlet exergy.

T4002 Presentation 10 (18:05~18:20)

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

Shiv Om Meena, **Dr. Manish Vashishtha**, Ankush Meena
Malaviya National Institute of Technology, Jaipur, India

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.

Poster Session

Afternoon, June 21, 2018 (Thursday)
Time: 15:50~18:50
Venue: C219
14 Poster presentations

T0051 Poster Presentation 1

Biodiesel production by methanolysis of rapeseed oil by using Li/ZnO as a catalyst

J. M. Encinar, J. F. González, N. Sánchez and S. Nogales
Extremadura University, Badajoz, Spain

Abstract- The aim of this research work was the production of biodiesel from rapeseed oil methanolysis, by using Li impregnated ZnO as an heterogeneous catalyst. With the aim of determining the optimum conditions of the process, the influence of some operating variables

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6	**CH0 601**	Shiv Om Meena, Dr. Manish Vashishtha	Determination of Nutrient Release from Neem Oil Coated Urea in Soil Domain Using Weight Loss Method
7	**CHO 365**	Bharath Velaga, Dr.Nageswara Rao Peela	Selective Production of Levulinic Acid from Bamboo Biomass Using Mesoporous Mordenite
8	**CHO 151**	Praful Bansod, Prof.S.SBarkade, Prof.Dinesh Bhutada	The synthesis of heterogeneous catalyst from the waste of thermal power plant for biodiesel production.

BROAD AREA: GREEN TECHNOLOGY			
28th December 2018		**Time: 04:45 to 06:15 PM**	**Room No. LTC-202**
Time: 04:45-5:15PM		**Chemcon Invited Speaker by Dr. O P Bahel, National Physical Laboratory, New Delhi**	
		Time: 05:15 to 06:15 PM	
S. No.	**Paper No.**	**Authors**	**Title of the Paper**
1	**CHO 481**	Aanchal Mittal, Sangeeta Garg, Shailendra Bajpai	Studies on the biodegradability of the PVA/starch composite films reinforced with grafted barley husk
2	**CHO 528**	Dr. Swapnil Dharaskar, Prof. Mika Sillanpaa	Phosphonium Based Ionic Liquids as Promising Green Solvent for Sulfur Extraction from Liquid Fuels
3	**CHO 529**	Swagata Das, Shubhalakshmi Sengupta , Papita Das	Effect of temperature variance on production of bioethanol using Saccharomyces cerevisiae
4	**CHO 567**	R.S.Achsah, M.Danish John Paul, N.Shruthi, R.Anantharaj	Esterification of Butyl Acetate using Ionic Liquid as Catalytic medium
5	**CHO 572**	Brijesh Kumar Yadav, Shishir Sinha	Effect of surface treatment on Thermogravimetric behavior of natural fibers
6	**CHO 573**	Manvendra Singh, G L Devnani, Shishir Sinha	Effect of alkali treatment on morpholgy, and crystalline behavior of coir fiber
7	**CHO 832**	Nikunj Jain, Padmasha Yadav, Anmol Gupta	Confined Space Bioreactor based Bioremediation

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CERTIFICATE

This is to certify that Professor/Dr./[✓ Mr.]/Ms. Shiv Om Meena

has presented a paper (Oral /Poster) entitled Determination of Nutrient Release from Neem Oil Coated Urea in Soil Domain Using Weight Loss Method

Co-authored with Dr. Manish Vashishtha

in International Conference on **"Seamless Chemical Engineering in Service of Humanity: Innovations, Opportunities & Challenges"** held at NIT Jalandhar during **December 27-30, 2018**.

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ABSTRACT VOLUME

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Controlled Release and Slow Release Fertilizers as Nutrient Management

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ABSTRACT

Nutrient management is closely associated with fertilizer type, application rate, application time, and application placement. For example, blueberry plants prefer am¬moniacal nitrogen rather than nitrate nitrogen for their growth and development. Most of the crops use both ammoniacal nitrogen and nitrate nitrogen. Proper nutrient manage¬ment should admit the "Four R's" of fertilizer use: apply the right nutrient, at the right rate, at the right time, and in the right place for the selected crop. This article shows that how to select the right fertilizer to enhance profitability and satisfy best management practices. There are many fertilizer sources available for commercial crop production. The characteristics of each fertilizer type determine whether its use poses an advantage or a disadvantage to a farmer. It frequently means that nutrients will not be available to plants when they need them. To deal with these challenges, the global fertilizer industry has been working to develop new fertilizers called controlled-release fertilizers (CRFs) and slow-release fertilizers (SRFs). These fertilizers have become more and more popular in recent years.Controlled-release fertilizers are typically coated or encapsulated with inorganic or organic materials that control the rate, pattern, and duration of plant nutrient release. Polymer-coated urea exemplifies CRFs. These fertilizers control the release of nutrients with semi-permeable coatings, occlusion, protein materials, or other chemical forms, by slow hydrolysis of water-soluble, low-molecular-weight compounds, or by other unknown means. Most importantly, the release rate of a CRF fertilizer is designed in a pattern synchronized to meet changing crop nutrient requirements.

Keywords: Slow-release fertilizers, Controlled-release fertilizers, Castor oil coated urea, Nitrogen release.

Endocrine Disruptors and Toxicological Implications

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ABSTRACT

Endocrine Disrupting Chemicals (EDCs) or most commonly referred to as Endocrine Disruptors (EDs) have been shown to interfere with physiological systems, i.e., adversely affecting hormone balance, or disrupting normal function, in the female and male reproductive organs. Although endocrine disruption is a global concern for human health, its impact and significance and the screening strategy for detecting these synthetic or man-made chemicals are not clearly understood in female and male reproductive functions.

A few in vitro and in vivo methods have been developed for determining whether a chemical is endocrine disrupting or not. Most results from in vitro and in vivo data are derived from assays which measure estrogenic and androgenic activity, and far less is known for progestogen effects. In order to solve the infertility problems in human beings the solution up to some extent through modern medical technology is Assisted Reproductive Technology (ART). ART is used to treat infertility by different means. In vitro fertilization is the most common technique which has been successfully used.

Keywords: Assisted Reproductive Technology (ART), Endocrine Disruptors, Infertility, Toxicological Implications

Chemical Methodologies 2(2018) 299-307

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Original Research article

Experimental Determination of Nutrient Release from Neem Oil (Azadirachta indica) Coated Urea

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Controlled release
Neem coated Urea
UV-Vis spectrometer

ABSTRACT

An accurate estimate of nutrient release pattern from controlled release fertilizer (CRF) is required both for manufacturers as well for farmers because of the fact that it helps them in understanding fertilizer potency and nutrient planning for the crops. Understanding the release pattern of different types of CRF under laboratory conditions as well as in the crop-field is essential in order to determine the fertilizer utilization efficiency on plant growth. The present work explains a simple experimental approach to understand the nutrient release from Neem coated urea (NCU). The coating of Urea with Neem oil (derived from seeds and leaves) inhibits the process of nitrification and reduces the formation of nitrates which in-turn will reduce N_2O emissions. It prevents the loss of urea in the soil. It also controls a large number of pests such as caterpillars, beetles, leafhoppers, borer, mites etc. Also, Neem coating is biodegradable and so it is environmentally-friendly as compared to many non biodegradable polymers used as coating materials in CRF.

UV-Vis spectrometer is employed to determine the amount of released nitrogen. The approach reduced analytical error by preventing sample dilution before measuring. According to laboratory results, the obtained UV-Vis spectrometer proved to be a handy and efficient equipment for studying the nutrient release behaviour from CRF. The release profile presents a sigmoidal shape which is in good agreement with the other works in the area reported in the literature. The obtained experimental results are also in tune with the criteria specified by European Committee for Standardization for CRF.

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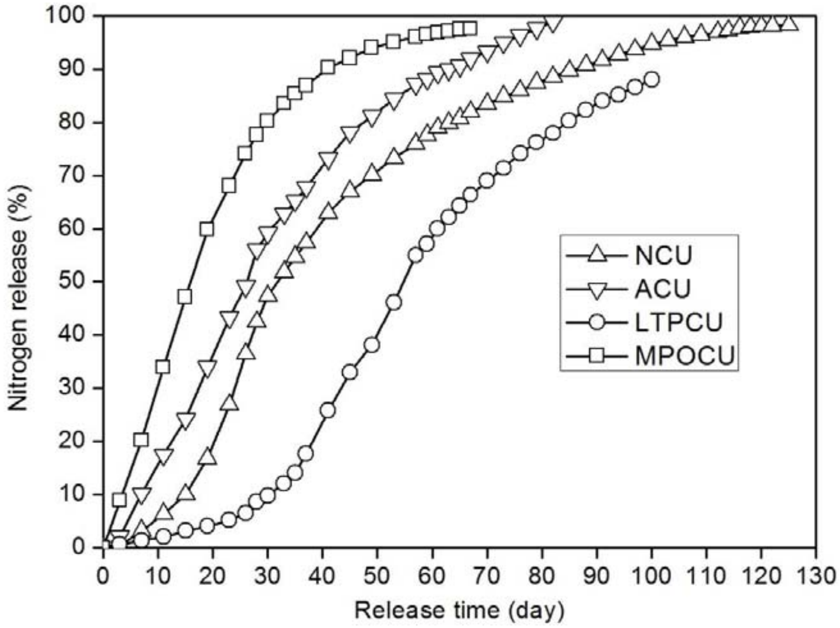
Graphical Abstract



Introduction

Soil fertility is primarily determined by three major elements namely Nitrogen, Phosphorus and 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 and 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, provide 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 uses [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 resulting in delayed transformation of ammonical nitrogen into nitrite nitrogen. Thus, it ensures slow and continuous availability of nitrogen regarding the crop growth. Coating urea with neem prevents its misuse as well as puts the fertilizer in slow release mode, nourishing the saplings for a longer period, and thus avoiding the repeated use of fertilizer. The process reduces pollution of groundwater. There is an increase in crop yield and efficient pest control management leading to savings. It also increases the shelf life of the product [6].

Current research is focused on CRF applications not only in the laboratory but also in the field crops. Majority of these studies focus on release pattern of CRF because it is has a direct bearing on the determining the effectiveness of these fertilizers on plant growth and in planning plant nutrient management. Goertz et al. studied the release of nitrogen from sulfur-coated urea, and the release was controlled by sulfur thickness [7]. Kochba and Gambash studied the release of nitrate from coated granule where the release occurred by diffusion of urea through a semi-permeable membrane [8]. Dai et al. evaluated the release of nutrient from two resin-coated N, P, K fertilizers [9]. Melissa et al. compared weighing and combustion techniques in studying the release of urea in the field [10].

Although the field tests provide a better demonstration of the nutrient release, however, it suffers from inherent constraints of being influenced by the variation in environmental conditions like temperature, soil moisture, soil pH, soil microbes population and porosity, etc. Thus, determination of nutrient release under laboratory conditions provides a convenient and useful approach to understand nutrient release mechanism. Medina et al. had pointed out that laboratory experiments were successful in predicting nitrogen release rate of slow release fertilizers [11]. Papangkorn et al. and Trinh et al. employed UV-Vis spectrometer in studying the urea release rate from polylactic acid coated and agrium coated urea respectively [12-13].

The present work is based on experimental determination of nitrogen release from NCU to obtain a better understanding of release behaviour. The results of present study are also compared to Nitrogen release from urea coated with other materials.

Experimental

Materials and Methods

NCU calibration curve: NCU (CAS 57-13-6), obtained from Chambal fertilizer and Chemical limited (CFCL) Gadepan, Kota (India), is used to prepare standards for calibration curve. Five NCU solutions were prepared with concentrations: 0, 100, 500, 1000, 2000, 5000, 10000*ppm*. UV-Vis double beam (Make Shimadzu, model UV-1800 available in the research lab of the Chemical

Engineering department) as shown in figure 1 is employed to measure the optical density of the above standards at a wavelength of 210 NM.

Figure 1. UV-1800 Spectrophotometer Double Beam (Malaviya National Institute of Technology, Jaipur)

Nitrogen release test: NCU is used in the nitrogen release test. The particle size distribution was determined for both uncoated urea and NCU using sieve analysis. For this analysis a sample weight of 342 gm was used for both uncoated and NCU. The resultant distribution is shown in figure 2.

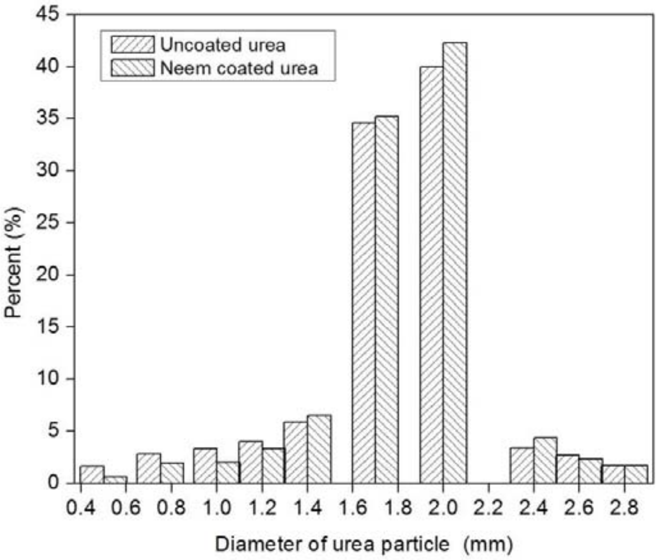


Figure 2. Uncoated and NCU particle size distribution

It can be seen from the figure that maximum particles are available in a diameter range of 1.7mm and 2.0mm. Also, it can be inferred from these results that particle strength also increases due to coating since the less number of particles of NCU are present in lower size distribution ranges. For conducting the release test, 2±0.001gm of NCU particles is immersed into 250ml of distilled water and placed at room temperature as shown in figure 3.

Figure 3. sample for release test

This particular amount of NCU is taken to ensure that urea concentration remains in the range of the calibration curve during the course of conducting the release test. After every 2-4 days, NCU concentration is determined by UV absorbance at 210 nm. Distilled water is added to the fixed point (250ml) before and after the sampling process. The released nitrogen is then calculated from the NCU concentration, and the experiment ends as the released nitrogen reaches 98.27%. Two repetitions were performed in the release test for the sake of attaining accuracy in the results.

Results and discussion

NCU calibration curve: Figure 4(a) shows a NCU calibration curve in distilled water constructedwith standards from 10 to 10000ppm. The obtained calibration curve is empirically given by the equation in which $y = 0.178x$ with $R^2 = 0.9949$ where x and y present NCU concentration in (ppm) and its absorption in mili absorption unit (mAU) respectively. The curve depicts linearity over a wide range, which helps the measurement of nitrogen release from NCU without dilution of samples.

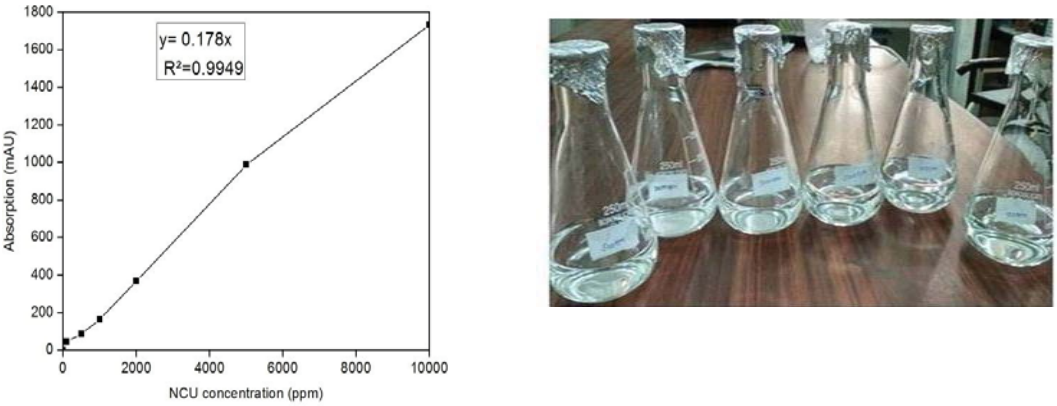


Figure 4. (a): Calibration curve for NCU at 210 nm, (b): Neem coated urea samples

Nitrogen release behaviour: The release profile determined experimentally for Nitrogen release from NCU is shown in figure 5(a). The release profile shows a sigmoidal shape and follows the diffusion stages as described by Shaviv et al. and Lu et al. [14, 15]. In first eleven days, the percent nitrogen release is 6.35%. This increases to 16.82% at the end of 19 days. Thus, up to 19 days the lag period or stage is observed, which is attributed to the fact that, 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 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.

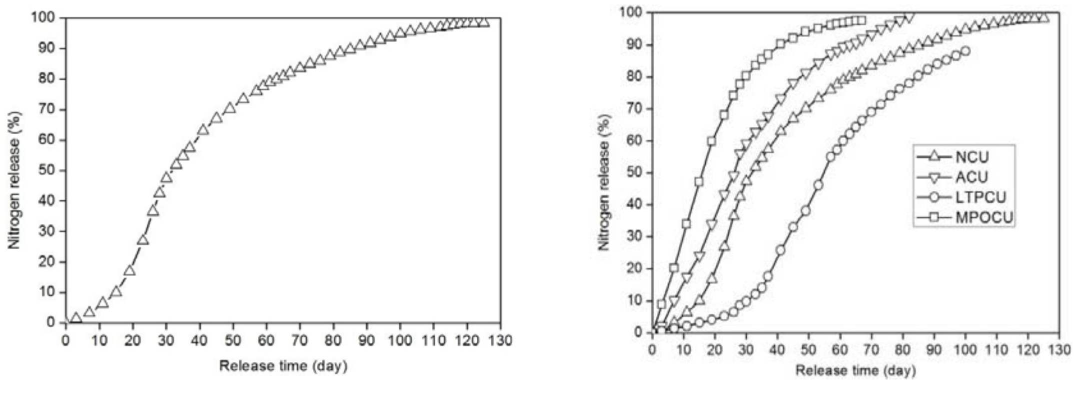


Figure 5(a). Nitrogen release profile in NCU, (b): Comparison of Nitrogen release in NCU with other Coated Urea

In other words, the lag can be due to the time needed for the establishment of a steady state between the flux of water entering the granule and the flux of solute leaving it. Once a steady state is achieved the volume change in the granule is negligible. In terms of thermodynamics, the system can be described as one with zero "net volume flux". Starting from 20th day, the release percentage rises rapidly and reaches to 89.65% at the end of 85th day. This corresponds to the second stage, called the constant release stage, which begins when a critical volume of saturated solution accumulating 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 85th day to 125th day, and the amount of nitrogen release reaches 98.27% at the end of the 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.

From the experimental data, a regression model is applied to the nitrogen release profile from NCU and the following equation is obtained:

1. $y = 10^{-9}x^6 - 5\times10^{-7}x^5 + 8\times10^{-5}x^4 - 0.0062x^3 + 0.229x^2 - 1.5827x + 1.9284$; $R^2 = 0.9984$

where, x and y represent the release time in days and Nitrogen release (%) respectively.

Experimental data for nitrogen release from NCU was compared with the Nitrogen release data available from the literature for urea coated with different coating materials viz. ACU (Agrium coated urea), LTPCU (Large tablet polymer coated urea) and MPOCU (Modified polyolefin coated urea) and the results are shown in figure 5(b) [16-18].

From the comparison, we can infer that neem coating is effective in increasing the release time of nutrient as compared to other coating materials since for achieving a representative 90% release the time taken is 40 days (MPOCU), 65 days (ACU), 90 days (LTPCU) and 100 days for NCU, thus NCU imparts a better controlled release character to the urea along with the added advantage of coating being biodegradable. Also the nutrient release from NCU (figure 5(a)) is in agreement with three criteria established by the CEN (European Committee for Standardization) [19]. CEN defines the conditions for a fertilizer to be described as slow-release if the nutrient or nutrients declared as slow-release meets defined conditions as shown in table 1 at a temperature of 25°C. The comparison of our data with CEN criteria is tabulated below.

Table 1. Comparison of experimental data with CEN Criteria

S.No.	CEN Criteria	Experimental results from NCU
1.	No more than 15% released in 24 hours	In 24 hours, percent of nitrogen released is 1.47% which less than 15%, so first criteria is satisfied.
2.	No more than 75% released in 28 days,	After 28 days, percent of nitrogen released is 44.44%, which is less than 75%, so second criteria is satisfied.
3.	At least about 75% released at the stated release time	Amount of nitrogen release is 98.27% within 125 days, so third criteria is satisfied.

The Nitrogen release rate is calculated and is shown in figure 6(a). The release rate increases and reaches a maximum at 30 days. After attaining the maxima the release rate decreases and becomes 0.75% /day at about 125 days , The release profile is comparable to the release pattern as shown by other coated fertilizers as shown in figure 6(b).

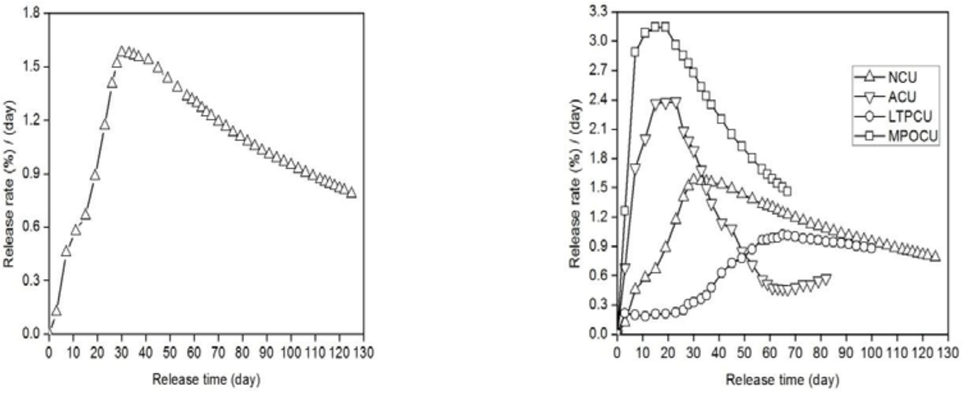


Figure 6(a). Release rate profile NCU, **(b).** Comparison of Release rate profile of NCU with other Coated Urea

Conclusion

In the present study Nitrogen release from NCU is carried out. Experimental results show that nitrogen release percentage follows a sigmoidal behaviour, first, it increase with time and later on becomes constant following a three stage process as discussed previously. The release data also show that NCU match the requirement for controlling release fertilizer. Besides, the use of UV-Vis spectrometer as a promising equipment, in studying the release behaviour is also highlighted.

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