Encapsulation of Urea Fertilizer in Fluidized Bed Coater Using Carboxylic Acids as Additives

By

Nida Zafar

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology

(NUST)

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Name: Nida Zafar

Reg No.: 00000170641

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Supervisor Name: Dr Muhammad Bilal Khan Niazi

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST) H-12
Islamabad, Pakistan

Dedication

This thesis is dedicated to my parents, especially to my father for his endless support, love and encouragement.

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Praise is due to **Allah** whose worth cannot be described by speakers, whose bounties cannot be counted by calculators, whom the height of intellectual courage cannot appreciate, and the diving's of understanding cannot reach; He for whose description no limit has been laid down, no eulogy exists, no time is ordained, and no duration is fixed.

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Nida Zafar

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Abstract

The global food production and consumption demand are increasing with increasing population. To fulfil this, demand a large amount of arable land is required. Unfortunately, the available land is diminishing due to industrialization and urbanization. Only about 10% of the land is available for cultivation. Due to the unavailability of land, the need of the hour is to provide a heavy amount of fertilizer to the crops. These fertilizers, in turn, will pollute the environment badly.

Nitrogen (N) is a crucial and important component of animal and plant cycle. Mankind is injecting reactive nitrogen into the environment either intentionally or unintentionally. As a result, it is affecting biodiversity, water quality, and human health and causing global warming. Synchronization of N supply with the crop demand is an efficient and profitable method in terms of crop production of N management. Urea fertilizer with N content of 46 % is used for further improvement and utilization for crop production. Nitrogen in Urea, when applied to soil, is lost in volatilization, Immobilization, Denitrification and Leaching. This loss will alter the bio-diversity. The development of Slow-release / Control release Fertilizer is to reduce these losses and altering nitrogen release according to the plant metabolic needs

Encapsulation of Urea Fertilizer with the polymeric coating is one of the solutions to the above-discussed problem. It controls the release rate of fertilizer by regulating N to the plant whenever required. It will reduce the multiple application of fertilizer and will minimize environmental pollution. This method will provide environmental security by minimizing health hazards and conserving bio-diversity along N management. Urea prills were coated with polymeric material and additives that will coat the prills by providing flexibility and strength to the coating. Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction XRD techniques were employed to check the bonding and cross-linking of polymer and additives. Crushing strength to check the liability of coating during handling and supply chain.

Keywords: Slow Release Urea Fertilizer (SRUF), Dissolution rate, Polyvinyl Alcohol, Starch.

Acronyms List

PVA	Polyvinyl Alcohol
S:P:AA2	Starch/PVA/Acrylic Acid 2wt.%
S:P:AA4	Starch/PVA/Acrylic Acid 4wt.%
S:P:AA6	Starch/PVA/Acrylic Acid 6wt.%
S:P:CA2	Starch/PVA/Citric Acid 2wt.%
S:P:CA4	Starch/PVA/Citric Acid 4wt.%
S:P:CA6	Starch/PVA/Citric Acid 6wt.%
S:P:MA2	Starch/PVA/Malic Acid 2wt.%
S:P:MA4	Starch/PVA/Malic Acid 4wt.%
S:P:MA6	Starch/PVA/Malic Acid 6wt.%
CRF	Control Release Fertilizer

Chapter 1-Introduction

The world population is increasing and demands increased production of food[1].It is expected that the population of the world will rise to 11 billion in 2050[2].Worlds consumption and demand of agriculture for food, fuel and feed are increasing at a rapid pace[3].Plants are the major means of life on earth. Eighty percent of proteins and ninety of energy human consumed are of plant origin[4].Current food production is not enough against the increasing global population. It is one of the main reasons that many people die every year due to hunger and malnutrition. To cope with this problem, it is essential to rising food production. Only 10% of the land is available for cultivation. Moreover, some are diminished for non-agricultural purposes for urbanization and industrialization. It is estimated that the land for agriculture which is now 0.26 hectares, will decrease to 0.15 hectares per capita in 2050. Plants need nutrients for their metabolic activity, optimum growth and production. Essential nutrients for plant growth are divided into micronutrients and macro-nutrients as shown in **Table 1**[5].

Table 1: Essential Plant Nutrients

Nutrients Supplied by air and water	**Nutrients Supplied by the soil system**		
Non-Mineral	**Primary or Macronutrients**	**Secondary**	**Micronutrients**
Carbon-C	Nitrogen -N	Calcium-Ca	Zinc-Za
Hydrogen-H	Phosphorus-P	Magnesium-Mg	Chloride-Cl
Oxygen-O	Potassium-K	Sulfur-S	Boron-B
			Molybdenum-Mo
			Copper-Cu
			Iron-Fe
			Manganese-Mn
			Cobalt-Co
			Nickel-Ni

From all the eighteen essential nutrients required by most of the plants Nitrogen-N, Phosphorus-P and Potassium-K are macronutrients. As these are required in larger quantities by the plants and found restraining in plant development and growth in soil system they are referred to as primary nutrients[5].Functions of primary nutrients are shown in **Table 2**.

Table 2: Functions of primary nutrients

Functions of Primary / Macronutrients in plants		
Element Name	**Function in Plant**	**Symbol**
Nitrogen-N	Promotes rapid growth, chlorophyll formation and protein synthesis	NH_4^+ NO_3^-
Phosphorus-P	Stimulates early root growth. Hastens maturity. Stimulates blooming and aids seed formation	$H_2PO_4^-$ HPO_4^{--}
Potassium-K	Increases resistance to drought and disease Increases stalk and straw strength. Increases quality of grain and seed.	K^+

1.2 Nitrogen (N):

Nitrogen high requirement in plant and its mobility in the environment makes it the most important and arguably nutrient[6]. Nitrogen has a noticeable role in plant metabolism[7]. It plays important role in increasing crop production and crop yield[8]. The increased use of N and good management practices in fertilizer increased the crop yield during the last fifty years[9].Nitrogen is playing a vital role in increasing the productivity of Pakistan's four major corpse.; cotton, sugarcane, rice and wheat. Deficiency of Nitrogen in Plants retards the plant growth, restricts the lateral bud growth and develops chlorosis (leaves colour changes). Proper growth of plants requires an optimum amount of Nitrogen. Less amount will retard the growth while higher amounts cause negative effects to the plants[10].

A plant takes nitrogen in the form of ammonium NH_4^+ and nitrate NO_3^- form. But this N is lost into the atmosphere or in the soil. Nitrogen cycle has the following different steps; exchange, nitrification, denitrification, volatilization, mineralization, immobilization, N_2fixation, and leaching[6]. The Nitrogen Cycle is shown in **Figure 1** [11].

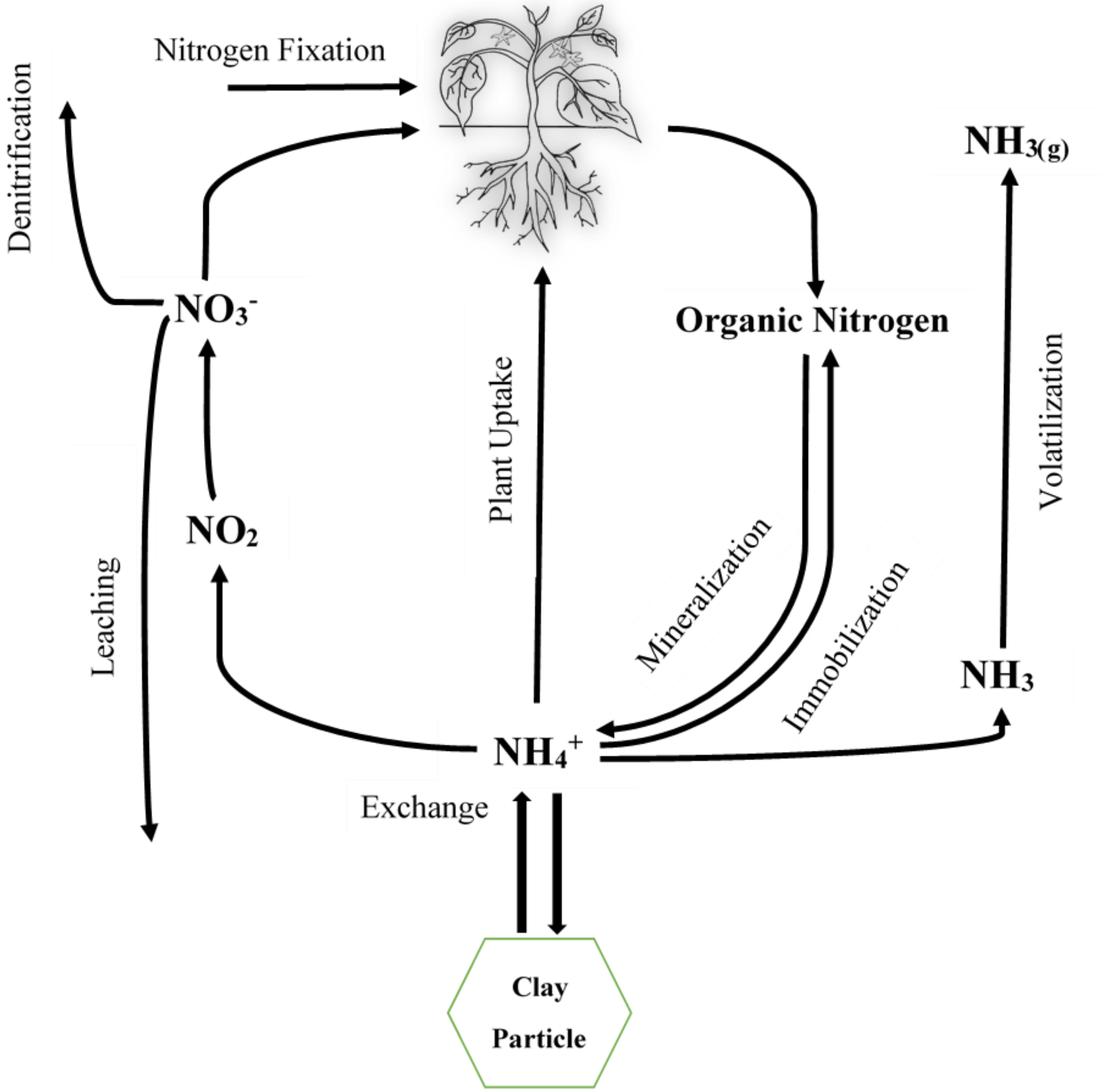


Figure 1: The Nitrogen Cycle

1.3 The Nitrogen Cycle:

1.3.1Mineralization:

The conversion of organic **N** into inorganic form **NH_4^+** and **NO_3^-** is called nitrogen mineralization. It usually involves 3 steps.

1) *Aminization:*

In the firststep, complex proteins are decomposed by heterotrophic soil organisms into simple amino acids and amines ($R-NH_2$).

2) *Ammonification:*

NH4 is released by the further decomposition of amines and amino acids by other heterotrophs.

$$R - NH_2 + H_2O \rightarrow NH_3 + R - OH + energy \qquad \text{(Eq. 1)}$$

3) *Ammonium Conversion:*

Finally, ammonium converts into nitrate through nitrification.

As it requires micro-organisms, soil conditions highly affect their activity. Aerobic conditions, moist and warm soil with neutral pH levels promotes the activity of micro-organisms. Amount of Organic matter present in the soil also affects this process[12]. As with the increased amount of organic matter, mineralization amounts are higher in soil and helps in constant availability of N in soil.

1.3.2 Nitrification:

Nitrification is the conversion of soil ammonium **NH_4^+** into nitrite **NO_2^-** and nitrate **NO_3^-**. This may take hours to weeks. It requires oxygen, so conversion cannot be possible in anaerobic conditions and water-logged areas. Nitrifying bacteria are responsible for this conversion. Then nitrite **NO_2^-** (toxic) converts into nitrate **NO_3^-** in saturated soils. Nitrification occurs more readily at pH 6.5 to 8.5 and 75 to 95 ºF temperature. It is a two-step process:

1. Ammonium oxidation by **Nitrosomonas**:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4\,H^+ \qquad \text{(Eq. 2)}$$

2. Oxidation of nitrite to nitrate by **Nitrobacter**:

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad \text{(Eq. 3)}$$

1.3.3 Denitrification:

It is the oppositeof nitrification and requires anaerobic conditions. In this step nitrate **NO_3^-** converts into Nitrogen **N_2** gas with the removal of Oxygen. Denitrification decreases the yield 4-5% nitrate loss /day from poorly drained soils. It enhances from increasing temperature from 40 to 80 ºF and then remains constant above it[13]. It usually occurs in moist soils and warm atmosphere. It is constant between pH from 5.6 – 8 and inhibited below 5.6.

1.3.4 Volatilization:

Volatilization is the loss of ammonium NH_4^+ in the form of ammonia NH_3 into the atmosphere. High temperature and low moisture level into the surface of the soil is its main reason. Ammonium NH_4^+ in the soil deprotonated into ammonia NH_3.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \text{(Eq. 4)}$$

This process will increase as the pH increases the conversion of ammonium into ammonia and is a problem in a less buffered solution. It increases with increase in temperature up to about 110 ºF, coarseness of the soil, increasing wind flow and N fertilizer application[14].

How to control volatilization losses:

- By applying Fertilizer in weather when soil-enzyme activity is low i.e. in cold weather.
- By injecting the fertilizer into the soil.
- In rain, when rain leaches fertilizer for the soil to absorb.
- By applying soil-enzyme inhibitor with the application of fertilizer.

1.3.5 Immobilization:

The biological conversion of inorganic **N** (**NH_4^+** or **NO_3^-**) into organic **N** is referred to as immobilization. It is the reverse of mineralization shown in **Figure 2**[15]. Nitrogen is immobilized as taken by the micro-organism and converts it into proteins and cell walls. As immobilization is controlled by micro-organisms, they require moist and warm soils with neutral pH. Nitrogen immobilization can be controlled by avoiding large quantity application of C: N organic materials and supplementing these with Nitrogen fertilizers.

As the micro-organisms die and decompose, immobilized N will convert into mineralized increasing the level of available N.

Minimizing Immobilization:

As immobilized Nitrogen loss is temporary but can be avoided by applying Nitrogen when the heavy residue is present or by applying where no residue to decompose is present, below the ground[15].

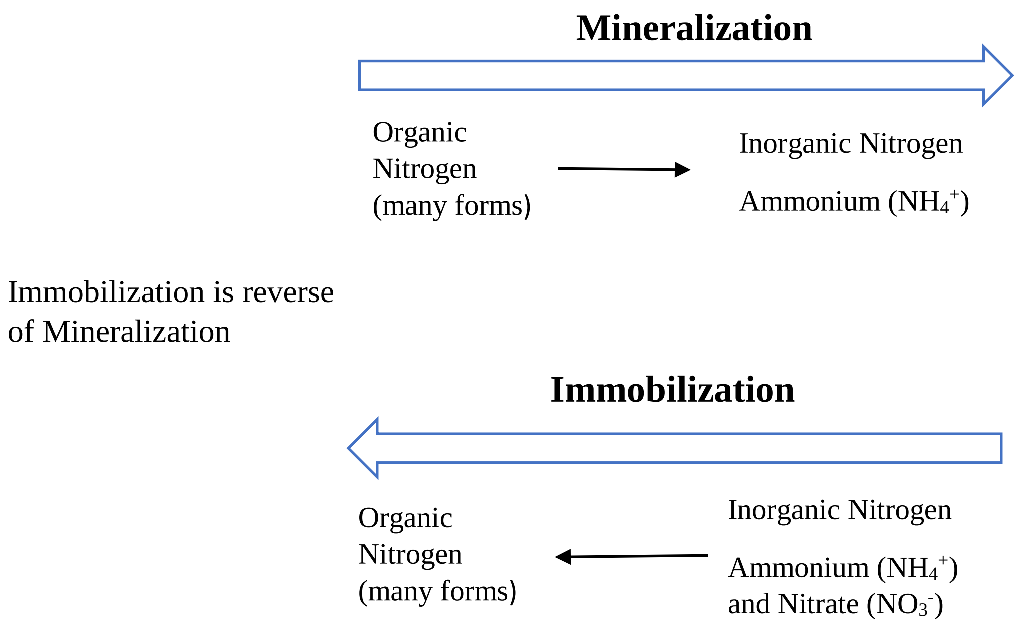


Figure 2: Comparison of Mineralization and Immobilization

1.3.6 Nitrogen Fixation:

Nitrogen fixation is the conversion of Nitrogen gas N_2 into the available forms of N that are taken by the plant. Three Nitrogen fixation processes are:

1) *Ammonia Fertilizer production:*

It requires natural gas, steam, oxygen and a catalyst to fix Nitrogen N_2 (g). So, it is highly dependent on the price of Natural Gas.

2) *Atmospheric Deposition:*

Atmospheric N fixation is through electrical discharge, through high-temperature combustion, human activities (e.g. industrial fixation of N to make organic fertilizer), and natural processes like volcanic activities) convert N_2 to NH_3 through thermal fixation. It is described in equation

Thermal nitrogen fixation

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \text{(Eq. 5)}$$

3) *Biological Fixation:*

Eighty percent Nitrogen in the air we breathe is converted to atmospheric Nitrogen N_2(gas) by micro-organisms[16].

1.3.7 Leaching:

Leaching is the penetration of nitrate through the soil into the root zone with water where it is unavailable to the soil. This problem persists in areas with heavy rainfall and sandy soils [15].

Minimization of Leaching:

- By the application of N in ammonia form using Nitrogen stabilizers
- By multiple application of Nitrogen

These four processes of Nitrogen loss can be either physical or biological. Leaching and Volatilization are physical processes that occur without microbial activity while Denitrification and Immobilization depend on microbial activity[15]. Microbes, in turn, are dependent on oxygen, moisture, the residue (food) and soil Temperature to sustain their population. When the temperature is less than 50 °F, microbial activity slows down at cold temperatures, denitrification and immobilization become insignificant.

Physical losses can occur year-round but typically Biological losses of Nitrogen occur in late spring through early fall.

Many efforts have been made so far to improve the quantity of available Nitrogen to the plant. One such attempt is multiple application of fertilizer according to the need or requirement of the plant. Second is the production of Slow-release Fertilizer that minimizes the release of Nitrogen and expected to release whenever required by the plant. It will not only helps in Nitrogen availability to plant but also will reduce the environmental problems[11].

The applied Nitrogen to the soil is not 100 % taken by the plant. It is lost into the environment or in the soil due to water and weather conditions. Volatilization, Immobilization, Denitrification and Leaching are major Nitrogen loss.

Chapter 2-Literature review

The global population is growing, so does the food demand and is predictable to become doubled till 2050. Due to increase in industrialization and urbanization, the available land for growing food is decreasing which result in a claimfor a large amount of fertilizer availability and most of them are harmful to the environment[1].To meet the increasing food demands with fertilizer which will not further pollute the environment, we need to develop fertilizer that is biodegradable. One solution to the problem is the production of controlled released fertilizer CRF.

2.2 Intelligent Fertilizer:

On application of fertilizer to the soil, most of the nutrient-like Nitrogen is lost to the environment through devolatilization, denitrification, and leaching. The use of "intelligent fertilizers" will help us to produce fertilizer that would be efficient enough to release nutrients when required by the plant with the lowest possible cost and easy availability[17].For the purpose of a slow release or controlled release,many coatingmaterials were used to coat urea granules or prills. The control release fertilizers either with organic and inorganic coating deliver the nutrients at a controlled rate,pattern, and duration which entirely depend on soil and climatic conditions. These fertilizers are not taken up by plants at once so making the bio available and provide nutrients whenever necessary but after some time of application[18].

2.3 Biodegradable Polymers for Urea Coating:

Biodegradable polymers are of great interest for many years as they do not pollute the environment and degrade by living microorganisms by chemical or enzymatic reactions, unlike non-biodegradable synthetic polymers that pollute the environment badly. Most synthetic polymers are not degradable and to make them so biodegradable polymers are associated with them such as natural polymers and aliphatic polyesters[19].

2.4 Starch and PVA as polymer backbone:

Starch is a natural polymer produced by plants such as corn potatoes and rice in the form of granules, a mixture of amylopectin (branched polymer) and amylose (linear polymer) which is a completely biodegradable polymer and protein can be used with non-biodegradable polymers [20].Starch is a low-cost polymer available in abundance with high purity cannot be used alone as it does not has high mechanical as well as processing properties so cannot replace whole petroleum hydrocarbons[19]. As starch is a water-soluble and brittle polymer so it is used and blended with other synthetic polymeric materials efficiently e.g. PVA polyvinyl Alcohol to improve its properties. The blend formed ratios give the best properties in terms of application with mechanical and thermal stability.

Both PVA and starch are biodegradable, so their blends are also regarded as completely biodegradable. PVA films are used for packaging material but due to their high cost and slow bio-degradation it is not used alone but is blended with starch which is a renewable and cheap polymer[21]. PVA and starch have high intermolecular and intramolecular interaction through hydrogen bonding due to the presence of (-OH) groups in both polymers. To increase the flexibility of blends or films and to decrease the melting temperature of PVA different plasticizers are being added.

2.5 Cross-linkers/Plasticizers:

Different cross-linkers/plasticizers are being used for this purpose to enhance the strength and flexibility of PVA/Starch. Citric Acid is an organic acid naturally present in foods such as citrus fruits and pineapples and is used as an additive with PVA/Starch blend[20].To improve the mechanical behaviour and water stability of starch it is cross-linked with citric acid. Citric acid is a poly (carboxylic acid) that contains hydroxyl groups as in starch, so form hydrogen bonds with starch and improves its water stability. Citric acid also improves the strength of Starch/PVA blend when compared with glycerol added to Starch/PVA blend[22].The concentration of citric acid also affects the tensile strength of the starch films when added below 5% less improvement due to lower interaction and cross-linking and above 5 % due to a decrease in the immobility of starch as dense bonding and cross-linking occurs. At 5 % of the added citric acid, it improves the bonding due to cross-linking and increase interaction between starch molecules, bondingand hence tensile strength[22].

Acrylic acid is another poly-carboxylic acid that is being used as an additive for Starch/PVA blends in the coating of urea prills or granules. Acrylic acid is a colourlessliquid, has an acridodour and is a simplest unsaturated carboxylic organic acid that is miscible with water and alcohol, chloroforms and ether. It is a by-product of ethylene and gasoline production. It can also be produced from hydrocarboxylation of acetylene. Naturally, it is produced in marine algae and in sheep's rumen fluid.

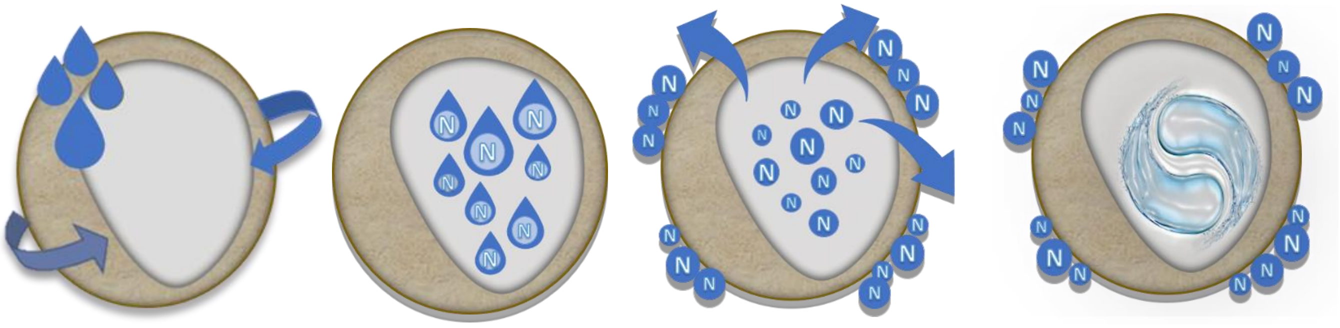
2.6 Plant Food.

The eco-friendly techniques and products play a leading role in life and development of living beings including human, animals and plants. There has been an exponential growth in world population that has now reached 7 billion approx.[23].Global food demand is also increasing and is expected to become doubled in recent years. The land that is already available is threatened due to Urbanization, desertification and land degradation due to flooding[24].To meet the increasing food demands a high amount of fertilizer is applied to the soil which causes environmental problems. The presence of higher amounts of NH_3 and NO_3^- in the soil will cause adverse effects on the environmental balance. To boost food production without these adverse effects several methods have already been applied[25].Controlled release fertilizer is one of the best solutions so far that will not only improve food production but will also alleviate environmental problems.

Starch is of interest, among natural polymers. Starch is a natural biodegradable polysaccharide polymer with good biocompatibility[26].It is easily soluble in water and hence unstable shape and mechanical properties. Due to complete biodegradability, renewability and low cost of starch it is a capable candidate for producing valuable materials. But due to poor processability, dimensional stability and mechanical properties it cannot be used directly[27]. PVA is a water-soluble synthetic and biodegradable polymer[28]. It has excellent mechanical property and good compatibility with starch. It is completely biodegradable in most of the enzymatic environments[29]. PVA and starch form strong interaction due to the presence of hydroxyl groups in them.

2.7 Cross-linker:

Cross-linking is done to further enhance the stability and mechanical strength of PVA-Starch blend. Poly-carboxylic acids such as citric acid, malic acid and acrylic acid are used for cross-linking. These are inexpensive and nontoxic crosslinkers[22].CA consist of 1 hydroxyl and 3 carboxyl groups. It is esterified with the carboxyl and hydroxyl in starch and PVA which results in improved water resistibility [26].Sameas CA, MA with 1 OH and 2 carboxyl and AA with 1 OH and 1 carboxyl consists of OH groups that form strong hydrogen bonds with OH in starch and PVA. The addition of additives-cross linkers increased the flexibility and strength of the PVA/Starch coating[30].Release Mechanism of Nitrogen from coated urea prills is shown in **Figure 3.**



(a) *Due to the influence of the soil temperature water penetrates the polymer coating and dissolves the nutrient core*

(b) *The moisture uptake and dissolution of the nutrient core results in buildup of osmotic pressure inside polymer coated granular/prills*

(c) *The osmotic pressure causes the nutrient solution to release through fissures, cracks or micropores in the polymeric coating*

(d) *The nutrients are fully released, and the coating disintegrates into the soil*

Figure 3: Release Mechanism of Coated Urea Prills

2.8 Mechanism of Controlled release from Coated Urea Prill:

Release mechanism important steps are: **(a).** Due to the influence of the soil temperature water penetrates the polymer coating and dissolves the nutrient core. **(b).** the moisture uptake and dissolution of the nutrient core results in a buildup of osmotic pressure inside polymer coated granular/prills. **(c).** the osmotic pressure causes the nutrient solution to release through fissures, cracks or micro-pores in the polymeric coating. **(d).**The nutrients are fully released, and the coating disintegrates into the soil[31]**.**

The release mechanism directly shows the effectiveness of the control release fertilizer. Its effectiveness depends upon the type of coating, agronomic conditions, the type of Control release fertilizer and much more.

Shaviv [32]and Liu [33] proposed a release mechanism from coated urea called multi-stage diffusion model.

2.9 Multi-Stage Diffusional model for CRF:

When coated fertilizer is applied to the soil, irrigation water penetrates the coating to the solid fertilizer core. It causes condensation inside due to the partial nutrient dissolution of the core. Subsequently, it builds up osmotic pressure inside the coating and granule/prill swells. Two processes could be observed after swelling of the core.

1) *Failure Mechanism or Catastrophic release:*

   When inside osmotic pressure surpasses the threshold resistance of membrane the coating will burst. It will cause spontaneously release of the core. It is observed mostly in frail coatings such as sulfur or modified sulfur coatings.

2) *Diffusion Mechanism:*

   If the coating will resist and withstands the developing osmotic pressure, fertilizer will release slowly. This slow release is by driving force due to pressure or concentration gradient across the physical barrier or maybe the combination of two. Polymer coatings are expected to depict this kind of behaviour e.g. polyolefin.

2.10 Effectiveness of Coated Urea Fertilizer over Conventional Urea Fertilizer:

Coated fertilizers supply nutrients better according to the requirements of the plant as shown in **Figure 4**. It provides nutrients to plant for optimal growth, efficiency and a reduction in leaching. One single and efficient application equals better value for money.[34]

It is beneficial to include controlled release fertilizers to plant nutrition program as 3E’s.

1. It improves nutrition delivery and **efficiency**
2. Improves **economy** by Reducing fertilizer, labour and resource costs, increase yield and generate more return on investment per season, and
3. Maintains **ecology** by Minimizing nutrient loss due to leaching, emission, volatilization
   and runoff.

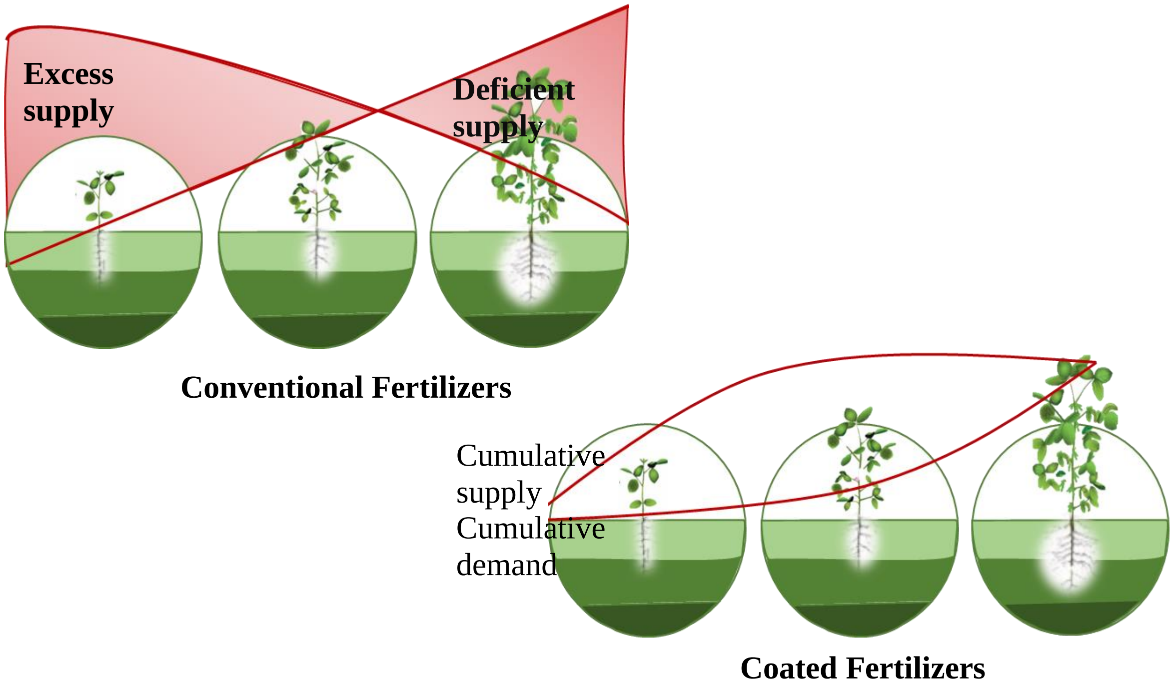


Figure 4: Comparison between Conventional and Coated Urea fertilizer

2.11 Advantages and Disadvantages of Control release fertilizers:

Advantages:

In addition to the 3E’s controlled release fertilizers inhibits hazardous emissions, seed toxicity, inhalation problems, dermal irritation, nutrient loss and leaf burning. They also improve germination rates, handling properties and soil quality[1].

Disadvantages:

There are some of the coating materials that are non-biodegradable and toxic to the soil and environment. They are expensive posing market issues. Some coating materials may alter the pH conditions of soil, which is undesirable. Storage facilities need modification to avoid pre-mature nutrient release through fissures and cracks of poorly handled damaged coated materials[35]. It may be vulnerable to changes in soil conditions like ambient moisture, bioactivity of the soil, its temperature, wetting and drying cycles of the soil. Changes in these conditions will affect negatively to the efficiency of coated fertilizer if specially calibrated for a specific crop.

2.12 Control release Fertilizer:

The term-controlled release fertilizer (CRF) is defined by ISO as: “Fertilizer in which nutrient release is controlled, meeting the stated release rate of nutrient and the stated release time at a specified temperature (ISO 8157:2015). These products are formulated to match the specific plant needs[34].

2.12.1Classification of Control release fertilizers:

Control release fertilizers are classified into the following according to Shaviv[32], Rose [36], Liu [33] and Trenkel [37].It is shown in **Figure5.**

Based on origin SRF or CRF can be divided into the following groups[1].

1) Organic Compounds:

Natural Organic compounds (animal manure, sewage sludge) and **synthetically produced nitrogen Fertilizers** (low solubility compounds). Condensation products from acetaldehyde and urea are included in synthetically produced low solubility compounds. These are further categorized as **biologically decomposing compounds** including urea formaldehyde. And **chemically decomposing** such as urea acetaldehyde /cyclo-diurea (CDU) and isobutyledene-diurea (IBDU).

2) Water soluble compounds with physical barrier:

Water soluble fertilizers with a physical barrier that control nutrient release. These are either **matrix of active fertilizer** nutrients dispersed on a continuum by hydrophobic material that hinders fertilizer dissolution or **coated granule/core** materials with the hydrophobic material. The controlled release matrix materials can be either **hydrophobic** such as rubber, polyolefin etc. or**hydrophilic**gel**-forming** called hydrogels. Coated control release is further subdivided into **organic coated fertilizers** by organic polymer materials such as **(thermoplastics, resins etc.)** and **inorganic coatings** like **sulfur** and other **minerals**. Coated control release fertilizers are more common as compared to matrices.

3) Inorganic low solubility compounds like **metal ammonium phosphates** e.g. KNH_4PO_4 and $MgNH_4PO_4$, and **partially acidulated phosphate rock** (PAPR).

In the review of the following literature, 3 different carboxylic acids were selected to coat urea prills. These acids will clearly reduce environmental pollution and soil deterioration by minimizing Nitrogen loss through leaching, volatilization and denitrification. Different carboxylic acids with 3 different wt. % of 2, 4 and 6 wt.% were added and their result was compared. The release rate is an important result to consider along with efficiency and crushing strength. Characterization was done using XRD, SEM and FTIR analysis.

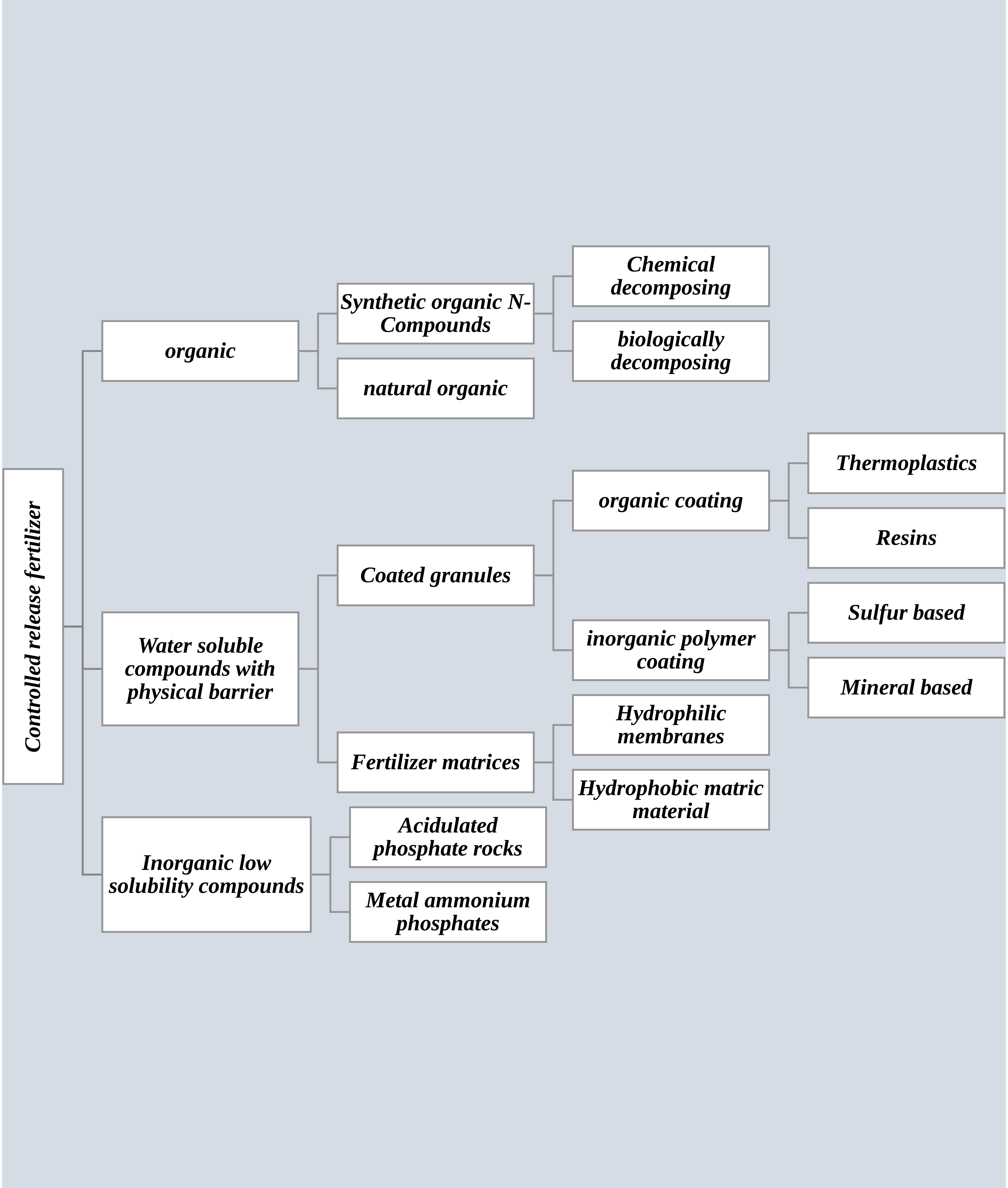


Figure 5. Classification of controlled release fertilizers[1]

2.13 Aim of research and Objectives

Pakistan is the agricultural country; the agricultural lands are very much dependent on fertilizer due to a rapid increase in population and increasing demand for Food items like Rice, Wheat, Fruit and Vegetables etc. Along with the above-mentioned issue, gas shortage also plays an important part in fertilizer shortages and in long-term food shortages. So, to meet up the above challenges this project in collaboration with HEC and FFC is very much relevant to national needs.

Objectives:

- Synthesis and characterization of coated urea using different additives in fluidized bed coater.
- Selection of the best combination of the polymeric coating based on release rate.
- Study the effect of different additives on the dissolution rate of slow release urea fertilizer.
- Pot test.

Chapter 3-Materials and methods

3.1 Materials and Methods:

Starch, PVA as primary components with Malic acid, Citric Acid, Aceticacid, concentratedHCl, P-dimethyl amino benzaldehyde from (Daejung Korea). Distilled water is used as a solvent. All chemicals were commercially available in analytical grade. Sieved urea prills of 2mm diameter from Fauji Fertilizer Company (FFC), Pakistan.

3.2 Method of coating solution formation:

The **s**tarch solution was prepared with continuous stirring until it becomes opaque and then plasticizers were added to the solution. PVA was added and well mixed for 15 min in distilled water and then heated at 98 °C for 45 min. The starch solution with plasticizers/cross-linkers and prepared solution of PVA were mixed together here citric acid, malic acid and acrylic acid is used as a crosslinker between starch and PVA and to make them better compatible for each other or to have better affinity due to the presence of -OH functional group in both. Then kept for 20 min at 40 °C on stirring to homogenize the whole coating solution. Heating plate with stirring is used for preparing the solutions. All the solutions were made in Distilled water.

3.3 Preparation of Coated Urea Prills [38]:

Urea prills from 1.5 to 2 mm in diameter were used for the experiment. Spray granulator YC-1000 mini spray granulator (developed by Shanghai Pilotech Instrument & Equipment Co., Ltd.) was used and material SUS 304 stainless steel & Bosiloricate Glass. For each batch/experiment, 200 g of urea prills was fed into the fluidized bed coater. The urea prills were placed into the feed section of fluidizing bed granulator and the air is blown through the heater at temp 80 °C to fluidize the prills through annular space between the inlet air section and feed plate. The pump is provided and operated at a desired speed that regulated the pressure of the atomizer from which the solution through flexible piping is delivered inside the feed section. The solution was sprayed into the granulator for some time then stopped and started again. This was done to avoid choking of the nozzle and for better coating and drying then again coating. This will prevent the agglomeration of the prills and attrition with the walls of the coater.Moreover,it will avoid the heavy duty of heater and compressor. This whole procedure was followed for about half an hour until then the whole prills batch was uniformly coated with the polymeric coating contain plasticizers malic, citric or Acrylic acid for this batch. The product then has taken off and stored in zip lock bags for further testing. The same procedure was adopted for all S:P:AA, S:P:CA and S:P:MA as described above in the solution preparation method. Coating Solution Composition is shown in **Table 3**.

Table 3: Coating Solution Formulation in wt. %

Sample Name	Starch	PVA	Acrylic Acid	Citric Acid	Malic Acid
S:P:AA2	10	5	2	-	-
S:P:AA4	10	5	4	-	-
S:P:AA6	10	5	6	-	-
S:P:CA2	10	5	-	2	-
S:P:CA4	10	5	-	4	-
S:P:CA6	10	5	-	6	-
S:P:MA2	10	5	-	-	2
S:P:MA4	10	5	-	-	4
S:P:MA6	10	5	-	-	6

3.4 Analysis of Slow Release Urea Prills:

Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared Radiation (FTIR), Crushing Strength, Release rate measurement wasperformed to analyze and compare results of coated and un-coated urea prills.

3.5 Scanning Electron Microscopy (SEM):

SEM (S-4700 Hitachi, Japan) was employed for the morphological study of coated and uncoated urea prills. Gold sputtering of 250 Angstrom was done on prills to cancel charge on it by Ion Sputtering Machine JFC-1500 of JEOL Ltd. It is shown in **Figure 6**.

The Key Components of a Scanning Electron Microscope are[39]:

3.5.1 Electron Gun:

It produces a steady stream of the electron beam of high intensity. It may be located at the very top or bottom of the SEM firing beam of electrons to the substance under examination. The electron gun is of two main types.

> **Thermionic guns:** It is the most common type, which applies thermal energy to high melting point filament, usually of tungsten. To coax electrons toward the specimen and away from the gun.
>
> **Field emission guns:** It creates a strong electrical field to pull electrons away from the associated atoms.

3.5.2 Lenses:

It uses a lens to create clear and detailed images. The lens here works differently. They are made of magnets instead of glass and can bend the path of electrons. These control the electron beam by precisely focusing them where they need to go.

3.5.3 Sample Chamber:

This is the place where a specimen to be examined are placed. This chamber must be insulated from vibration and sturdy for keeping the sample still to produce clear images. These machines are sensitive to vibration and preferable to install on the ground floor of the building. Sample chamber also moves the specimen at different angles to take different images without constantly remounting the object[40].

3.5.4 Detectors:

It detects the various ways in which an electron beam interacts with the sample. Electrons which are dislocated from the outer surface of a sample are Everhart-Thornley detectors register **secondary electrons**. These detectors can produce the most comprehensive images of an object's surface. Other detectors, such as X-ray detectors and backscattered electron detectors, can state about the composition of a substance.

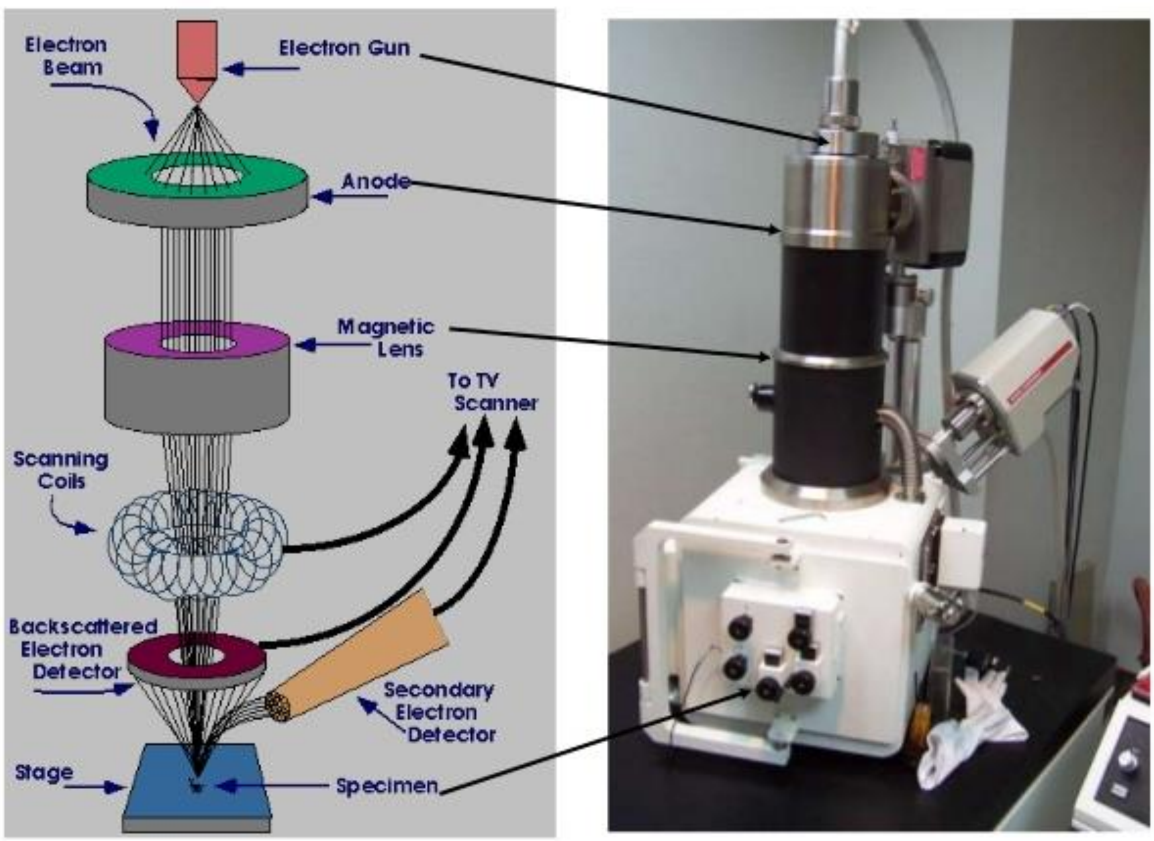


Figure 6: Scanning Electron Microscope

3.5.5 Vacuum Chamber:

Vacuum is created to minimize the interference of electron beams generated by an electron gun from air particles in the atmosphere**.** These particles block the path of the electron beam and are knocked out of the air and onto the specimen, which would distort the surface of the specimen.

3.6 Fourier transform Infrared Spectroscopy (FTIR):

FTIR was done with Perkin Elmer Spectrum 100 spectrometer, wave number /cm ranging from 400 to 4000/cm. Urea prills either coated or uncoated was crushed and mixed with Kbr powder to make pellets. These pellets were analyzed for the presence of bonds and required cross-linking. It is an easy way to detect the presence of certain molecules. In infrared spectroscopy, molecules have internal vibrations of specific frequencies. These frequencies occur in the infrared region of the electromagnetic spectrum: ~ 4000 /cm to ~ 200 /cm.

A sample when placed in a beam of infrared radiation, it will absorb radiation at frequencies corresponding to molecular vibrational frequencies but will transmit all other frequencies. The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is the infrared spectrum of the material. As different materials yield different infrared spectra due to different vibrations so, identification of a substance is possible. Furthermore, the absorptionfrequency, it is possible to determine whether various chemical groups are absent or present in a chemical structure[40]. Block diagram of its components is shown in **Figure 7** and its correlation in **Figure 8.**

Components of FTIR:

3.6.1 Source:

IR energy is emitted by a black body source. A beam of energy passes through an aperture which also controls the amount of energy presented to the sample and ultimately to the detector.

3.6.2 Interferometer:

The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3.6.3 Sample:

The beam hits the sample after entering in sample compartment. It is either transmitted or reflected from the surface; depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

3.6.4 Detector:

The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

3.6.5 Computer:

The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

Infrared Source → **Interferometer** → **Sample** → **Detector** → **Signal and data processing**

Figure 7: Basic Components of FTIR

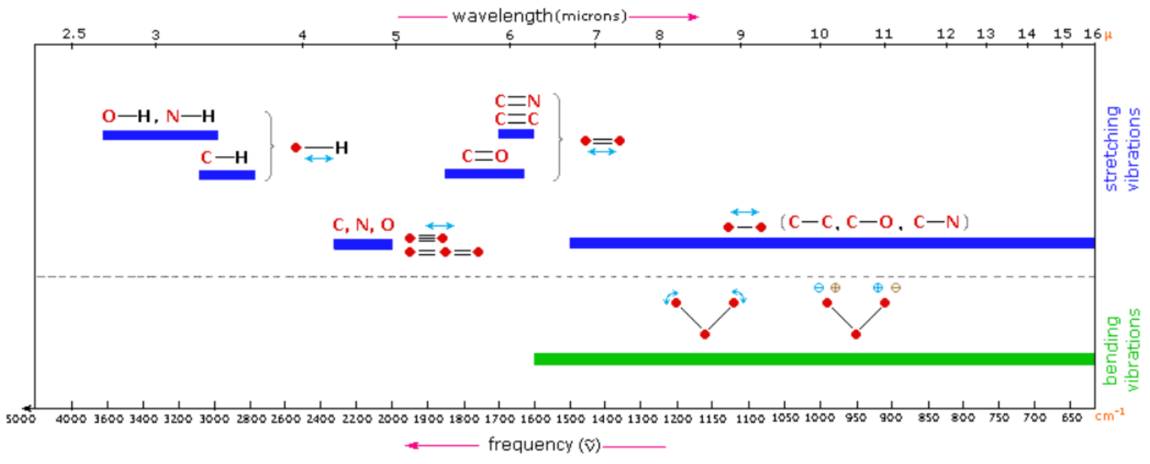


Figure 8:FTIR correlation table [41]

Wave numbers listed in cm^{-1}.

3.7 X-ray Diffraction (XRD):

XRD of coated and uncoated urea was performed with STOE Germany to check the crystallinity of synthesized formulations. Scanning angle was varied from 20° to 60 °. Step size and step time were taken as 0.4 degrees& 1 second respectively. Radiation used for characterization was of Cu K α-1[42].

This analytical technique is efficient in the determination of solid solution composition, grain size, lattice constants and the degree of crystallinity in a mixture of crystalline and amorphous substances[43].It is based on monochromatic constructive interference of X-rays and a crystalline sample.

It consists of 3 main elements:

3.7.1 X-ray tube:

X-rays are generated by cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed towards the sample. When electrons have enough energy to dislocate the inner shell electron of the sample, characteristic X-ray spectra are produced.

3.7.2 Sample holder:

The sample rotates in the path of the collimated X-ray beam at an angle θ. An arm to collect the diffracted X-rays and rotates at an angle of 2.

3.7.3 X-ray detector:

Due to the interaction of the sample with incident rays, constructive interference is produced when Bragg's Law (n λ=2dsinθ) conditions are satisfied, shown in **Figure 9**.These diffracted rays are then processed and counted after detection. By scanning the sample through a range of 2θ angles, due to the random orientation of the powdered material all possible diffraction directions of the lattice should be attained [40].

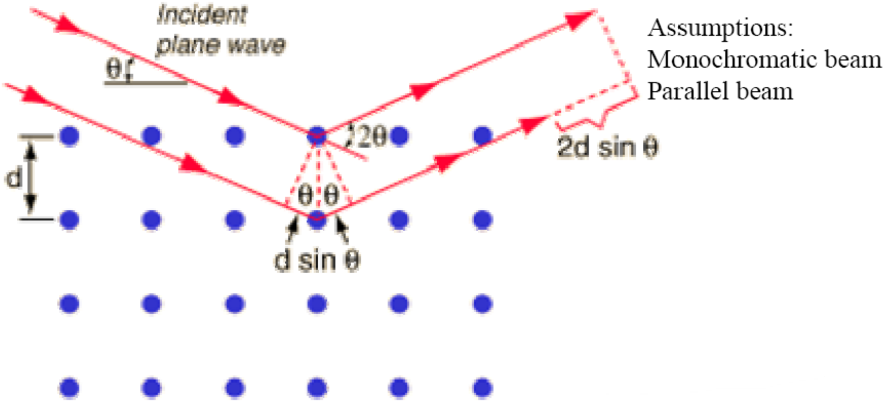


Figure 9: A Schematic Bragg's reflection of a crystal

By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing.

3.8 Crushing Strength:

It is required force to crush the particle. It is the measure of the resistance of the coating to fracture during physical handling throughout the supply chain. Universal testing machine (AGX Plus) is used for this test. This machine is used to find the tensile strength and compressive strength of materials. It measures how resistant a material is under compressive load, as shown in **Figure 10**. Average prills size randomly were chosen and placed under metal plunger of machine and readings were recorded with the help of software. The graph showed the limit after which the coating fractured and then urea prill crushed. Stress was noted and that was assigned as the limit of the prill to crush under stress. Generally, this test was performed on the major particles size of urea prills [44].

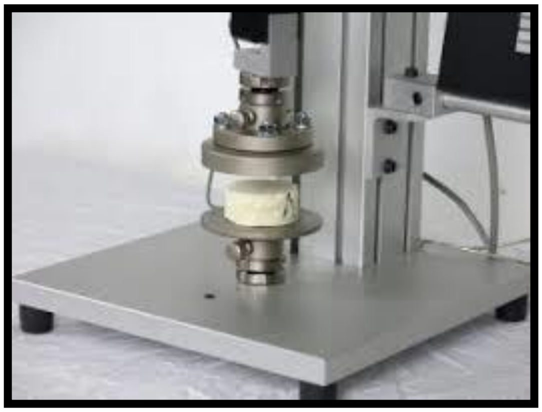


Figure 10: UTS Compression test

3.9 UV-Visible Spectrometry:

It operates by passing a beam of light through a sample and measuring the wavelength of light reaching a detector. The wavelength gives valuable information about the chemical structure and the intensity is related to the means quantity or concentration and number of molecules. Analytical information can be revealed in terms of absorbance, a reflectance of energy in the wavelength range between 160 and 3500 mill micron and transmittance[45].The absorption of the sample was measured with GENESYSTM20 UV-Visible spectrophotometer. Initially, the calibration curve was drawn. Standardized solutions of analytical grade urea (20 ppm, 40 ppm, 60 ppm, 80 ppm, and 1000 ppm) were prepared to get the slope from the drawn calibration curve. The absorbance was measured. After that calibration curve was drawn by plotting graph between known urea concentration and absorbance. Following the test, the protocol was used to find the dissolution rate of prepared coated samples.

The predetermined electromagnetic radiations of UV radiation: 300 to 400 nm and Vis radiation: 400 to 765 nm.

3.9.1 Lambert-Beer Law:

When the light with intensity I_o is directed at a material and light with intensity I is transmitted a relationship is established called Bouguer -Beer law or Lambert-Beer Law. As shown in **Figure 11**.

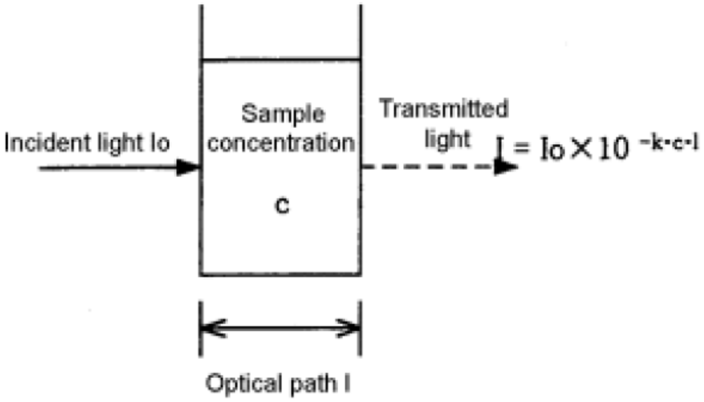


Figure 11: Lambert-Beer Law

In this instance, the value I/I_o is called transmittance (T) and the value I/I_o*100 is called transmission rate (T %). The value log (1/T) = log (I_o/I) is called absorbance (Abs).

$$T = I/I_o = 10^{-kcl}$$

$$Abs = \log(1/T) = \log(I_o/I) = -kcl$$

K=proportionality constant, l=length of the path through cuvette in cm. Absorbance is proportional to concentration. When l= 1cm and c= 1 mol/l, the proportionality constant is called molar absorption coefficient denoted by $\boldsymbol{\varepsilon}$. It is the characteristic value of material under certain conditions[40].

3.10 Test protocol:

10 grams of sample urea prills were taken in a 5 litres glass beaker filled with de-ionized water.10 ml of sample aliquots was taken from the centre of beaker at time internals of 3min, 6 min, 9min, 12min, 15min, 30min, 1hr and 2hr and dilution was done to 50 ml for absorbance measurement using UV-Visible Spectrophotometer method. The beaker was put on stirring for 15 sec before collection of sample.10 ml sample was collected from 50 ml flask containing diluted sample into the 50ml volumetric flask and then add 1ml HCl (1:1) &5 ml p-Dimethyl Amino Benzaldehyde solution in it along with de-ionized water to make it up[46]. Finally, absorbance was noted using a wavelength of 418 nm to calculate the unknown concentration of coated urea, release rate and efficiency.

$$\text{Conc. urea(ppm)} = \text{Absorbance } \div \text{Slope from the calibration curve}(\boldsymbol{\varepsilon}) \quad \text{(Eq. 6)}$$

$$\text{Efficiency (\%)} = \left(\frac{C_U - C_{CU}}{C_U}\right) x100 \qquad \text{(Eq. 7)}$$

Where,

C_U and C_{CU} are the concentrations of urea (ppm) in the uncoated and coated samples at 9 min, respectively.

Table 4: Urea Concentration (ppm) Vs Absorbance (a.u.)

Sr. No.	Urea (ppm)	Absorbance (a.u.)
1	0	0
2	20	0.024
3	40	0.051
4	60	0.072
5	80	0.096
6	100	0.12

Absorptivity or “a” or Slope of the curve=0.0012

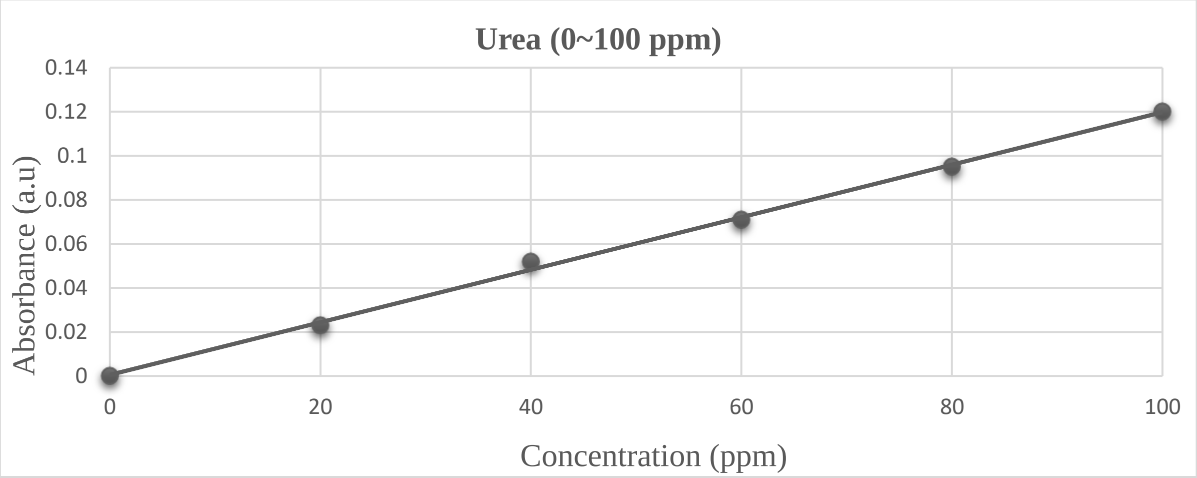


Figure 12: Urea calibration curve.

Chapter 4-Results and discussion

4.1 The release rate of Coated Urea Prills:

This technique was used to find out the release rate and pattern of the coated urea prills. Coated and uncoated urea prills were immersed in the distilled water. The concentration at different time interval was measured in ppm from the absorbance equation (Eq. 6). It was required that the coated urea prills should have the low release of total Nitrogen into the water than uncoated. Amount of Nitrogen release was determined as a function of time at 25 ºC. The time at which the concentration does not change was the halt time of the experiment. Urea prills were completely dissolved at that time. All samples were subjected to the same procedure. At last, the efficiency of coated and uncoated urea prills was found at 9 min using equation (Eq. 7). Nitrogen release from the different coating is shown in **Table 5**.

Table 5: Concentration of N. release from Uncoated/Coated Urea Prills in water at 25 °C

Time	**Uncoated**	**Coated Samples Concentration in ppm***								
		AA2	**AA4**	**AA6**	**CA2**	**CA4**	**CA6**	**MA2**	**MA4**	**MA6**
3	72.75	13.5	21.9	60.25	17.75	13.58	6.08	29.41	2.75	33.43
6	100	15.75	44.41	68.58	28.58	32.75	36.91	49.41	52.75	51.08
9	100	23.92	72.75	100	39.41	68.58	100	75.34	77.12	78.5
12	100	100	100	100	61.9	100	100	100	100	100
15	100	100	100	100	62.75	100	100	100	100	100
30	100	100	100	100	100	100	100	100	100	100
60	100	100	100	100	100	100	100	100	100	100
120	100	100	100	100	100	100	100	100	100	100

**** Starch and PVA is present in all samples***

4.2Surface Morphology:

To study the microstructure of the coated and uncoated urea prills, Scanning Electron Microscopy (SEM) technique is used[47]. SEM machine (S-4700 Hitachi, Japan) was used for analysis to see the surface morphology of coated and uncoated urea with different plasticizers. The resulting images of the surface morphology of uncoated are discussed here.

4.2.1 SEM analysis of Uncoated Urea Prill:

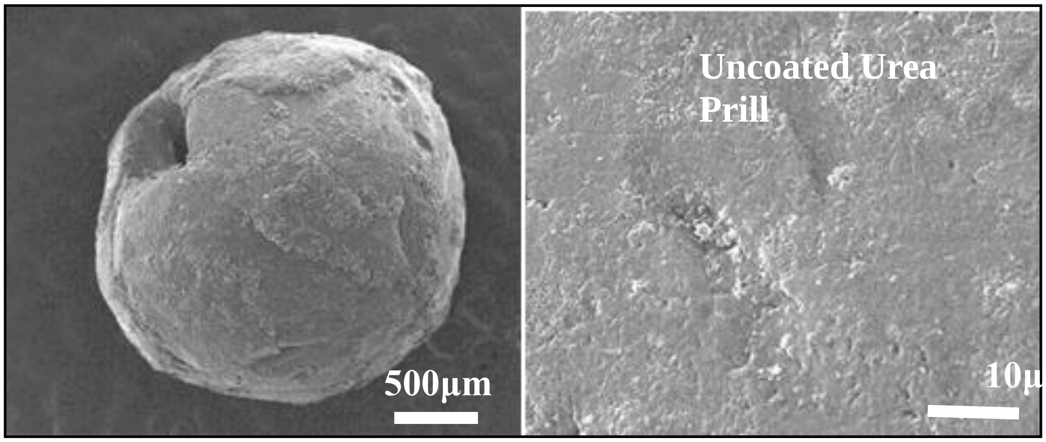


Figure 13: SEM micrograph of Uncoated Urea

The Surface micrograph of Uncoated Urea prill is shown in **Figure 13**. The surface of the urea prill is showing the large pointy crystals with the fine ones that are tightly cemented on to the surface. Some of the gaps and pores are also visible. Since urea production involves agglomeration that means theoretically onion layers are illustrated. However, the ring formation is not clearly visible here. The surface looked rough with clear pointy crystals [48].

4.2.2 SEM micrographs of Starch/PVA/Acrylic acid blend:

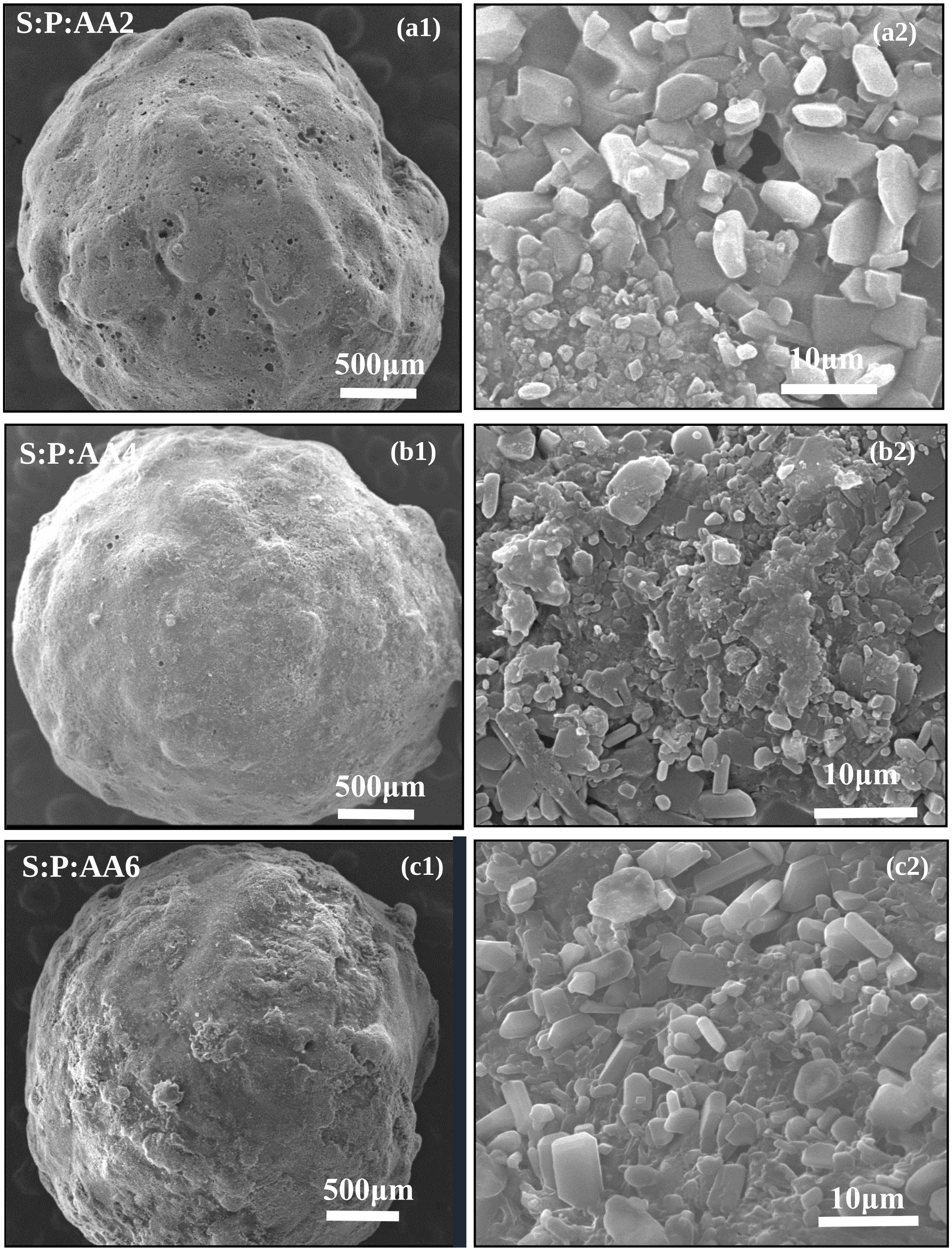


Figure 14: SEM micrographs of Starch/PVA/Acrylic Acid Coated Urea

In **Figure 14 (a1, a2)** SEM micrographs of **S:P:AA2** are shown. It shows the random bigger slabs; some eddy particles can also be seen. The coating layer is dense with some pores and cavities. Few areas are best covered and dense but some of the portions are edgy. The edgy part is the indication of the appearance of the urea surface. As urea surface is visible that means coating at that region is not intact with the surface. The urea prills are uncovered. With the increase in the percentage of the coating as shown in **Figure 14 (b1, b2)** the slabs become fewer with pointy edgy particles on the surface. It is covering the whole surface without any gaps and cavities. This is the indication of good coverage of urea prill. Here the coating is quite dense without the pointy exposed surface of urea through gaps. Some agglomeration due to non-uniform contact between urea surface and coating. Relative to **S:P:AA4, S:P:AA6 in Figure 14 (c1, c2)** is showing similar microstructure due to the same material**.** It has a surface with pointy edges and a small random region of compact and intact covering. The pointy edgy particles are due to urea surface appearance through pores. This shows that with an increase in the concentration of coating thickness cracks starts to propagate on to the surface. These cracks will expose the urea surface. due to urea [48].

4.2.3 SEM micrographs of Starch/PVA/Citric acid blend:

The SEM micrographs of Starch/PVA/Citric acid show a dense, homogenous, smooth and continuous surface without the appearance of any pores. The white granules are may be starch granules, and it may reduce the mechanical properties due to its brittle behaviour[30]. In **Figure 15 (a1, a2)** no projections and wrinkles are visible which is an indication of no significant phase separation between the PVA and Starch. It also indicates that citric acid enhances the binding of PVA/Starch forming a dense and homogenous film. Lower concentrations of citric acid do not show an appreciable change in morphology. Starch/PVA/Citric acid cross-linked urea and blank urea do not show an appreciable change in morphology. The outer coating at this concentration is smooth and showing fully dispersed coating. The amount of granules appearing more or less is the indication of compatibility of the mixture [49].Increasing the concentration of citric acid in the blend is increasing the agglomeration on the surface of the urea prill shown in **Figure 15 (b1, b2).** By increasing the concentration, the projections due to citric acid and pores may be due to agglomeration are also started appearing at this point. The gaps appeared are exposing urea surface. However, with further increase in the concentration of citric acid, the projections become more prominent. These edges are may be due to the exposed surface of urea through gaps, cavities or imperfections in the coating as shown in **Figure 15 (c1, c2)**. In comparison with the change in concentration, the sample **S:P:CA2** is showing dense and complete coverage of urea prill. The absence of the edgy pointy particles is the major indication of good coverage.

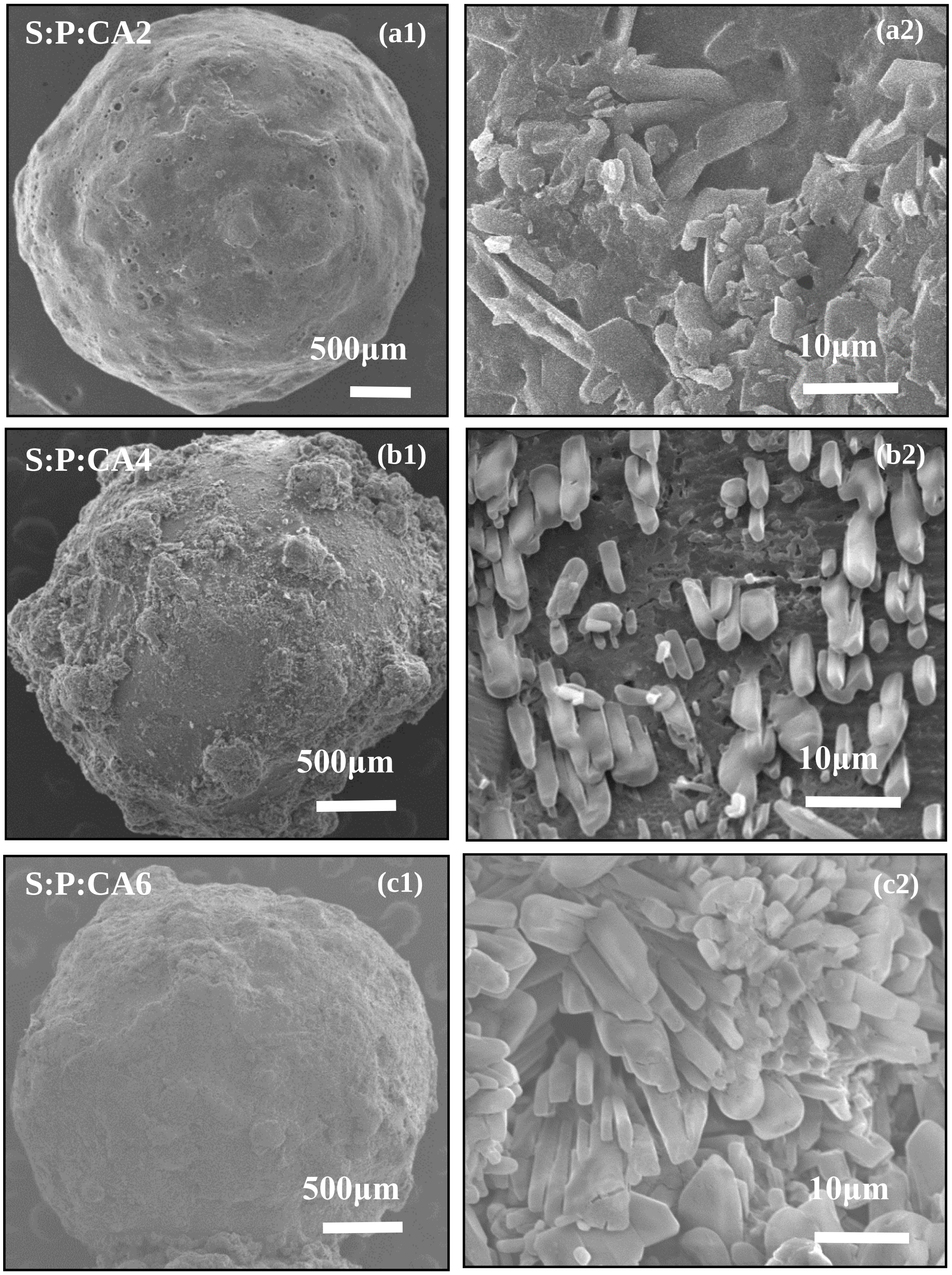


Figure 15: SEM micrographs of Starch/PVA/Citric Acid Coated Urea

4.2.4 SEM micrographs of Starch/PVA/Malic acid blend:

SEM micrographs of the combination of Starch/PVA/Malic acid are shown in **Figure 16**.

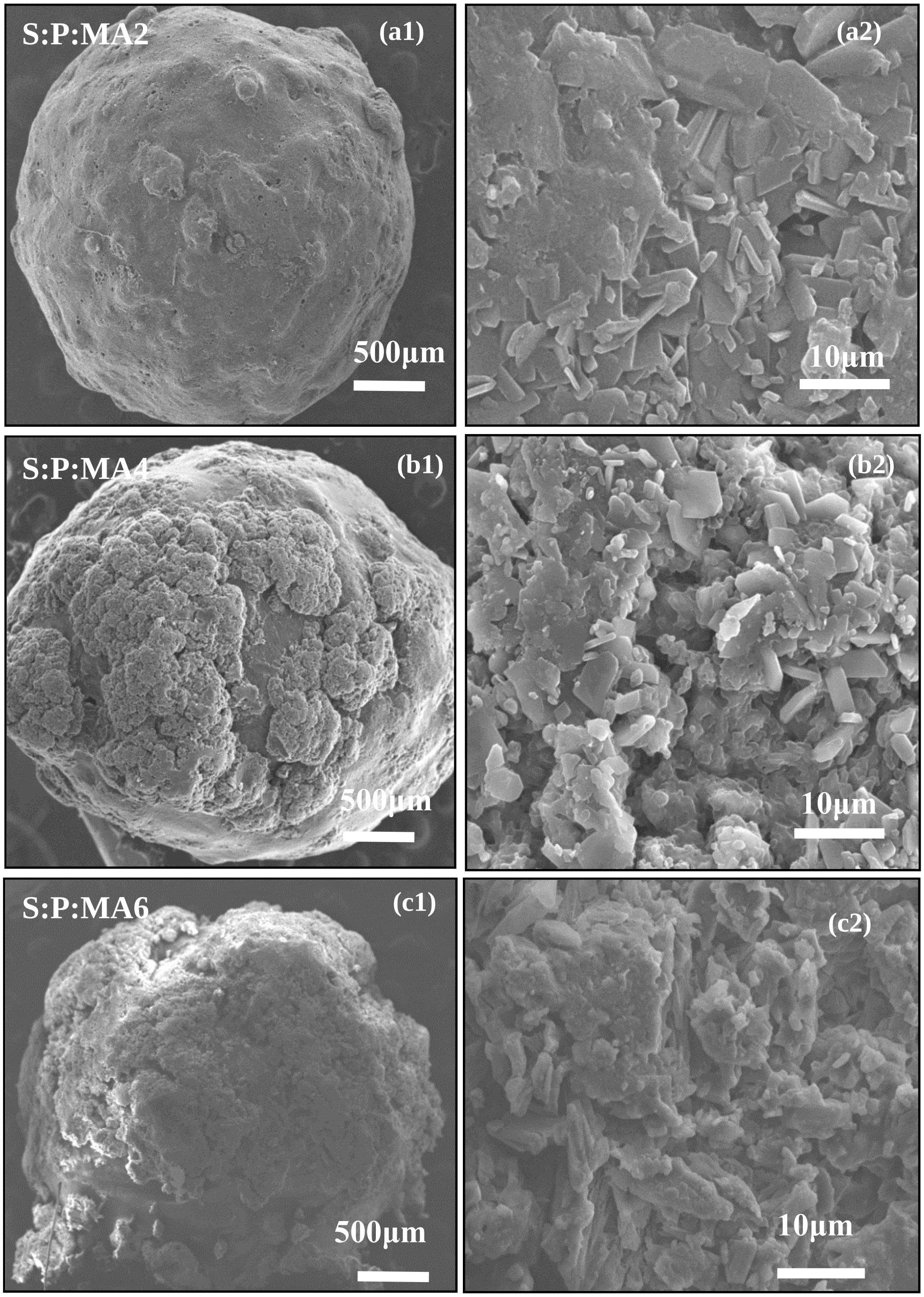


Figure 16: SEM micrographs of Starch/PVA/Malic acid coated urea

With a lower concentration of malic acid in **Figure 16 (a1, a2),** the surface of the urea is partially covered with a dense coating.

However, some of the regions are showing spikes or edges of the urea surface. This is showing incomplete coverage of the surface. Some of the pores and cavities can also be seen which will represent un-efficient coating to some extent.

In **Figure 16 (b1, b2)**, unlike lower concentration of malic acid shown in **Figure 16 (a1, a2)**, an increase in the concentration of malic acid is filling the gaps and crevasses. This is forming a dense cluster of particles on the surfaces surprising the appearance of urea surface. There may be due to the thorough contact between the urea surface and the coating. This intact coating will prevent and will control the release rate better. This can be further verified with the strength of the coating through the crushing strength test.

If the concentration of the plasticizer further increases in the coating solution the urea surface starts to appear. It is shown in **Figure 16 (c1, c2).** One assumption is taken here as with an increase in the amount of plasticizer will reduce the intact behaviour of coating with the surface. Here plasticizer may agglomerate creating big holes for urea surface to appear. The increased concentration of malic acid may have produced cracks in the coating. These cracks will show the edgy particles indicating the uncoated region. This may affect the release rate badly.

Conclusion on SEM analysis of Coated Urea Prill:

Layering and agglomeration on coated urea can be seen from the SEM micrographs which are the indication of the coating **Figure 13**. Uncoated urea has an irregular surface. The best coating and covering are achieved with the samples S:P: AA 2 wt.% and S:P: CA 2 wt.%. Their surface is smooth, homogenous, continuous and dense with no visible pores. It indicates that the citric and malic acid improves the binding of starch and PVA. All the plasticizers are cross-linked with starch and PVA and are well dispersed [30]. The rough outer layer in the coated sample also prevents the mechanical damage of the coating and enhance its water retention capability in the soil [50].

Starch granules have an elliptical shape and it has good compatibility with PVA[51].It forms a dispersion with the PVA so will give good covering properties. Starch is a brittle polymer with poor mechanical properties. Additives/Plasticizers are added to it to improve its mechanical properties and making it flexible [52].

The coated sample S:P:CA2, S:P:CA2 and S:P:MA4 are showing the best-coveringproperties. This result is further verified through Release rate and Crushing Strength analysis.

4.3Fourier Transform Infrared (FTIR) Spectroscopy:

FTIR spectrum was carried out to find the interaction between starch/PVA polymers with plasticizers and is shown in **Figure 14-16**.

All spectra were recorded at an ambient temperature of 25 ºC and wavelength ranging from 400 – 4000 /cm. The figure shows the first layer FTIR band of Uncoated Urea powder. The bond of primary amine was observed that correspond to the stretching of N-H in urea. This band is comprised of two peaks first is at 3442 / cm and another at 3348 / cm. Two more bands of high intensityappear, one at 1677 / cm corresponds to the C=O and another 1624 / cm for vibrational stretching of N-H bond. Vibrational stretching of the C-N bond of Urea was observed at 1465 / cm. A band of the slightly low intensity of 1468/ cm was also observed and corresponds to the vibrational stretching of the C-N bond of urea. These absorption peaks are consistent with relatively published results[53].

The band that corresponds to the vibration of primary amine N-H is the bond in urea, disappeared. This indicates that the coating on urea was successfully done and covers urea. The slight band shift in carbonyl was also seen which the indication of strong interaction through hydrogen bonding between the carboxyl group of starch and amino group of urea.

The FTIR spectrum shows that with increasing the ratio of Plasticizers by keeping polymer ratio same the coating and hence bonding becomes strong. This was verified by the absence of primary amine band in the spectrum.At 400- 1500 /cm or fingerprint region, all the usual peak of urea samples and the samples look very similar.

4.3.1 FTIR spectrum Analysis of Starch/PVA/Acrylic acid:

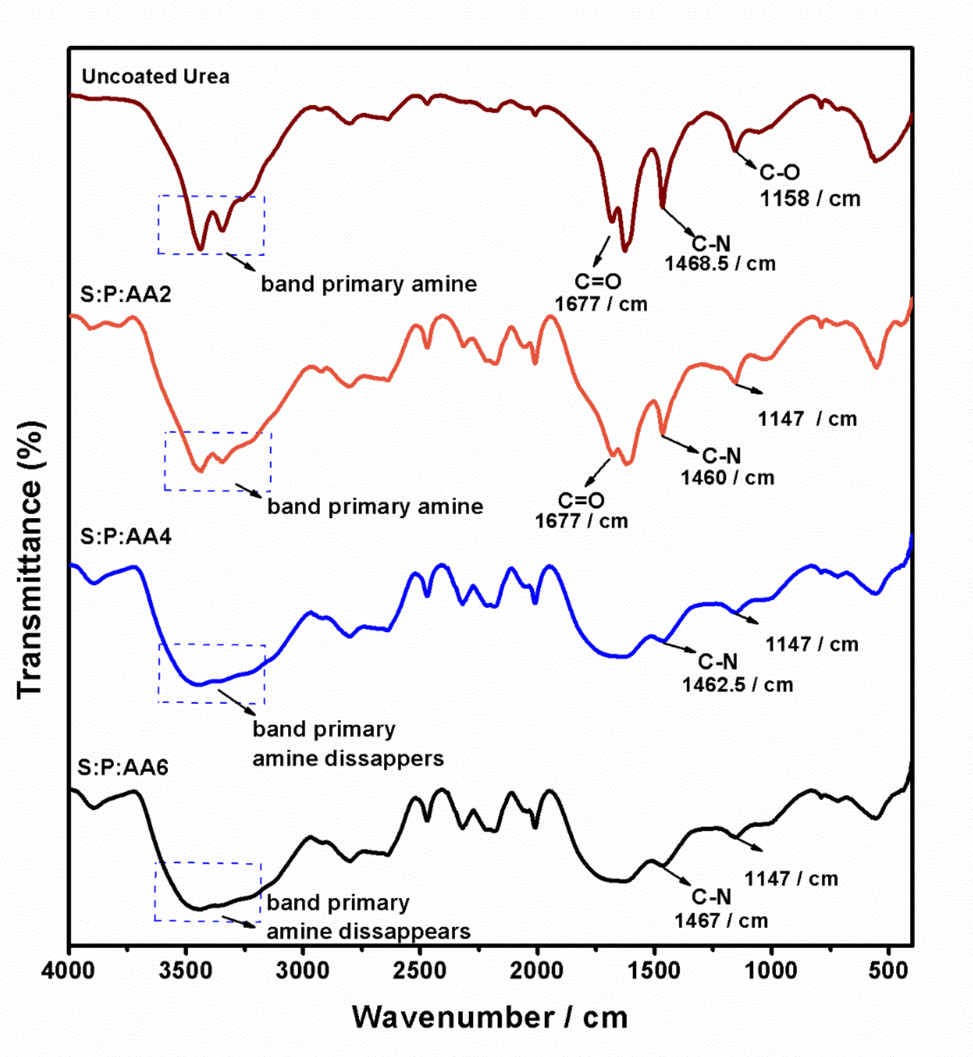


Figure 17: FTIR spectrum of Starch/PVA/Acrylic acid

The FTIR spectrum of Starch/PVA/Acrylic acid is shown in **Figure17.** All the characteristic peaks of Amine bond -NH_2 remain almost unchanged in **S:P:A2.** As urea contains primary amine it shows N-H symmetric and asymmetric stretch in the region of 3400- 3250 /cm. Two bands 1) from 3400-3300 /cm and another from 3330 – 3250 /cm. N-H bend can be seen in amines at 1650-1580 /cm. N-H bend in urea is at 1628.5 /cm [54]. C-N stretch is at 1468 /cm for urea and is shifted due to cross-linking of urea with Starch/PVA/Acrylic acid.The band at 1147 /cm is crystallinity dependent and is characteristic for PVA. It appears in S:P:AA2 and is weakened with the increase in the concentration of the acrylic acid.It might due to the deformation of the structure of PVA after cross-linking.

With the addition of acrylic acid which is carboxylic acid,it shows a strong broad band of O-H in the region 3300-2500 / cm. However, due to the crosslinking of Starch/PVA with a carboxylicacid, the amine band becomes less sharp. The decrease in sharpness and broadening of the band is an indication of Hydrogen bonding between the carbonyl bond of starch and OH of PVA. The reason that the O–H stretch band of carboxylic acids is so broad is that carboxylic acids usually exist as hydrogen-bonded dimers [54]. Carbonyl stretching C=O is also seen in the region of 1760-1665 /cm. In **Figure17**it is indicated at 1677 /cm. With the addition of Carboxylic acid, it gets broadened with increasing concentration of acrylic acid.

4.3.2 FTIR spectrum Analysis of Starch/PVA/Citric acid:

In **Figure18** the spectrum for urea contains primary amine it shows N-H symmetric and asymmetric stretch in the region of 3400- 3250 /cm. Two bands 1) from 3400-3300 /cm and another from 3330 – 3250 /cm. N-H bend can be seen in amines at 1650-1580 /cm. N-H bend in urea is at 1628.5 /cm [54]**.**The decrease in intensity from 3200-3500 /cm after cross-linking with citric acid is ascribed to the hydroxyl groups as shown in **S:P:CA2**,**S:P:CA4** and **S:P:CA6**. This decrease and broadening of peaks are increasing with increasing Citric acid content of the mixture. This shows that the bound water and hydroxyl groups were eliminated and there is a fall in –OH content. A new peak at 1619 /cm indicates the formation of –C=C– structure in PVA chains [55].O-H bend at 1444.5 /cm of carboxylic acid can be seen in **S:P:CA6**.The band appearing at 1781 /cm correspond to ester carbonyl and carboxyl bands in **S:P:CA4 [22].**

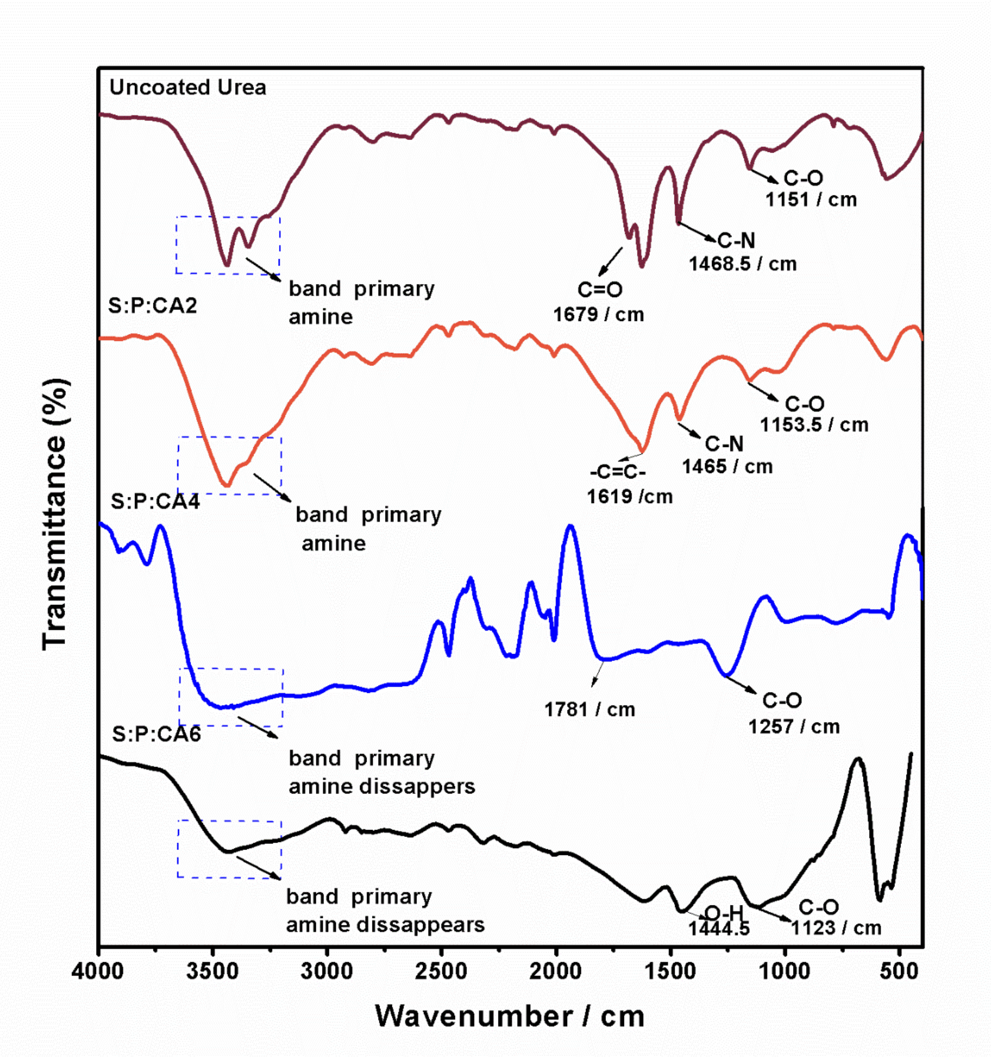


Figure 18: FTIR spectrum of Starch/PVA/Citric acid

4.3.4 FTIR spectrum Analysis of Starch/PVA/Malic acid:

Figure19 shows the spectrum of Starch/PVA/Malic acid blend. There is no new bond appeared in the spectrum but the bonds C=O and C-O broadened. This broadening of bonds is may be due to cross-linking between the carboxyl groups of malic acid and OH present in starch or PVA. This broadening may also be attributed to the formation of Hydrogen bonds here. In **S:P:MA2** the peaks are almost the same as uncoated urea. With the increase in concentration and with the coating, the broadening due to OH also can be seen. In S:P:MA the peaks are more broadened due to the availability of more OH and carboxyl groups. However, due to the crosslinking of Starch/PVA with a carboxylicacid, the amine band becomes less sharp. The decrease in sharpness and broadening of a band is an indication of Hydrogen bonding between the carbonyl bond of starch and OH of PVA. The reason that the O–H stretch band of carboxylic acids is so broad is that carboxylic acids usually exist as hydrogen-bonded dimers [54].

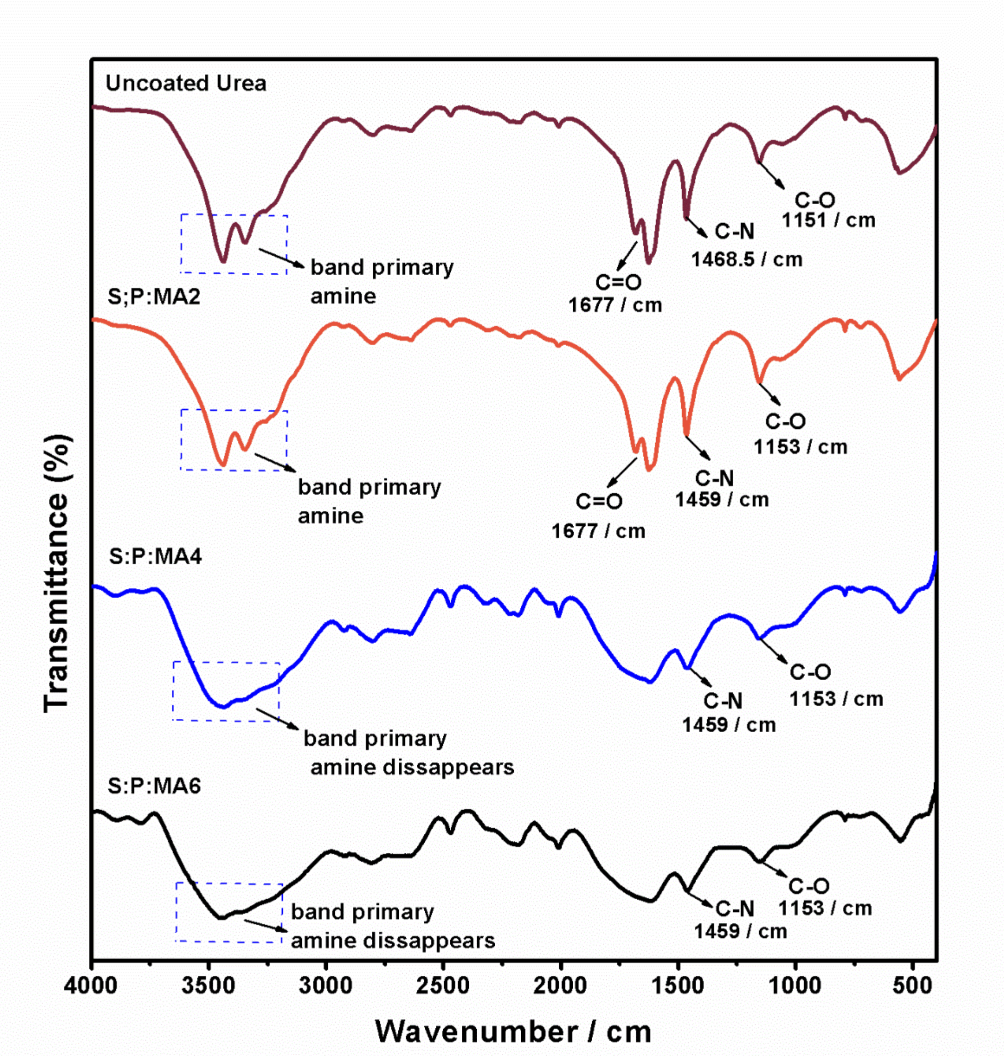
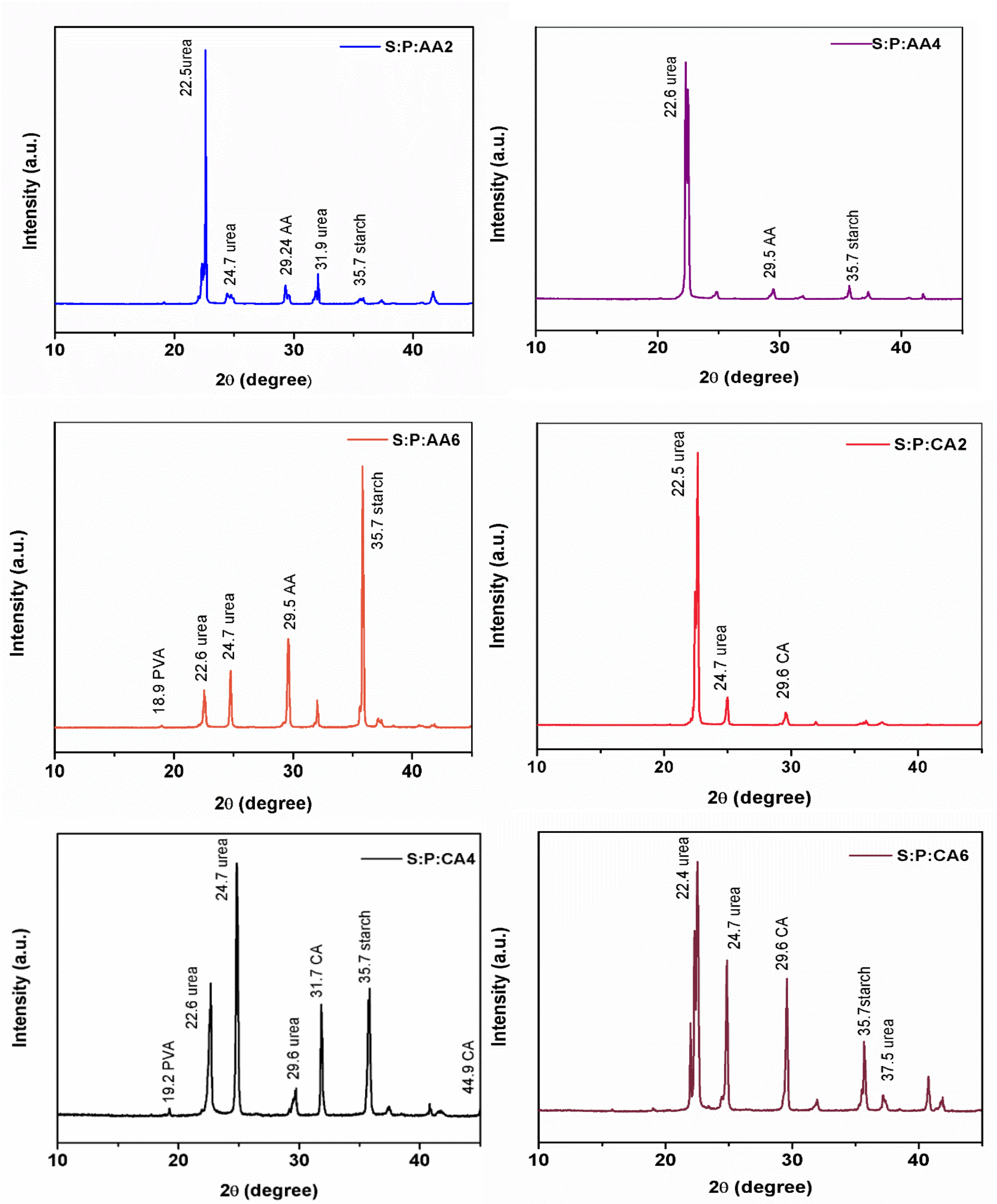


Figure 19: FTIR spectrum of Starch/PVA/Malic acid

4.4 X-ray Diffraction (XRD) Analysis:

XRD was done with the help STOE Germany Machine and shown in **Figure 20**. It was done to examine the crystallinity of the coated material. Scan angle was varied from 2 θ = 20º to 60º. Xrd results are showing a characteristic peak of urea in coated and uncoated samples. Along with urea peaks, peaks of plasticizers can also be seen. Some of the peaks related to the coating materials like starch, PVA, Acrylic acid, Citric acid and malic acid peaks.



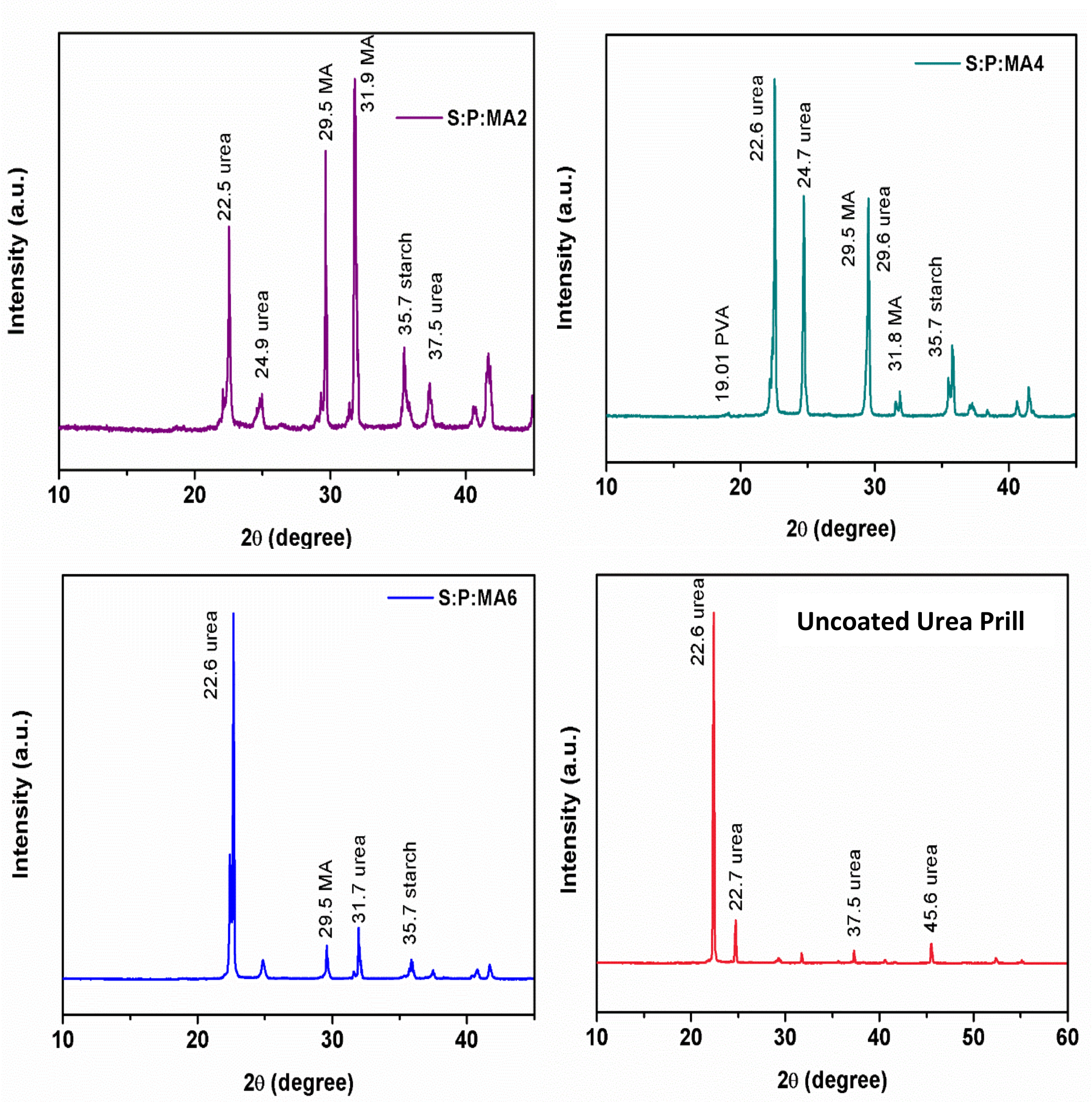


Figure 20: XRD Pattern of Coated / Uncoated Urea Prill

The reason that no new peaks or very low new peaks were seen in the coated urea prills, it may be said that no new phases were formed or no deformation in the structure took place during the coating process[17].

Urea show characteristic peaks at 22.5º, 24.7 º, 31.9 º, 37.5 º and 45.6 º.Starch shows a peak at 35.7 º.PVA shows a peak at 19.2 º.Acrylic Acid at 29.5 º.Malic acid at 31.9 º.Citric acid at 31.7 º and 44.9 º.The figure shows the respective peaks of all coated samples.The absence of PVA peak in XRD spectrum is an indication of the destruction of crystalline structure with an increase in amorphous [56].Some of the peaks reorient due to crosslinking, resulting in improved crystallinity [57].This type of peaks can be seen in case of **S:P:CA** and **S:P:MA** in **Figure .S:P:MA 2** and **S:P:MA4** areshowing an increase in intensity with increase in the concentration of MA.However, in S:P:MA6 the peaks are not as high.This change may be due to the restriction of chains with further increase in MA. Increase in peaks intensity is showing improved crystallinity due to increased crosslinking.Increasing concentration of the crosslinker is showing high-intensity peaks accordingly. Starch is a semi-crystalline in nature and its peak also disappeared in many of the coatings due to deformation of its structure.

4.5Crushing Strength:

Crushing strength is the required force to crush the particle. It is measured by applying pressure to individual prill of specified size until it fractures. To find crushing strength equal size of prills must be analyzed as with the increase in size strength changes. It is the measure of the resistance of the coating to fracture during physical handling throughout the supply chain[44].UTS (universal testing machine) is used for this test. The pressure force was applied by the metal plunger attached to the machine. The crushing test results are shown in **Figure 21**.

The crushing strength greatly depends on the chemical composition of the coating. Increase in crushing strength indicates the physical barrier that retards water [58]. Water absorption has a negative effect on coated prills. It disintegrates the prills, forming them sticky forming agglomerates. Crushing strength is the measure of mechanical resistance of the fertilizer to resist the stresses during handling chain [59].

With the coating, the crushing strength and impact resistant of coated urea improved as compared to untreated urea [58].Acrylicacid, Citricacid, Malicacid, Starch and PVA are coated to improve the mechanical strength of Urea prill.

From **Figure 21** it can be concluded that some of the coating combinationsgive satisfactory results**.** Whereas it is clear from Figure 21 that **S:P:AA2** and **S:P:CA2** blends showed highest crushing strength, and this can be verified from SEM images. The minimum percentage of the coatinggives good coverage which leads to good crushing strength. Higher concentration leads to higher cross-linking restricting chain mobility and hence decreasing tensile strength [22]This may be due to good dispersion between polymers and plasticizers. With the increase in concentration may increase thickness but causes agglomeration. Increase in coating with lead to the stiffness, immobility and decreases flexibility in return which damages coating easily[60].It is clear from **Figure 21** that increasing concentration of the plasticizers does not give good crushing strength and compatibility. This decrease in crushing strength may be due to the restriction in the movement of polymer chains. Increased concentration of plasticizers restricts the movement of the polymeric chains. Hence, the flexibility of the coating decreases and then mechanical strength[61]. Less flexibility and strength may induce cracks in the coating during handling and transportation [62].These can be supported through SEM micrographs and Efficiency results.

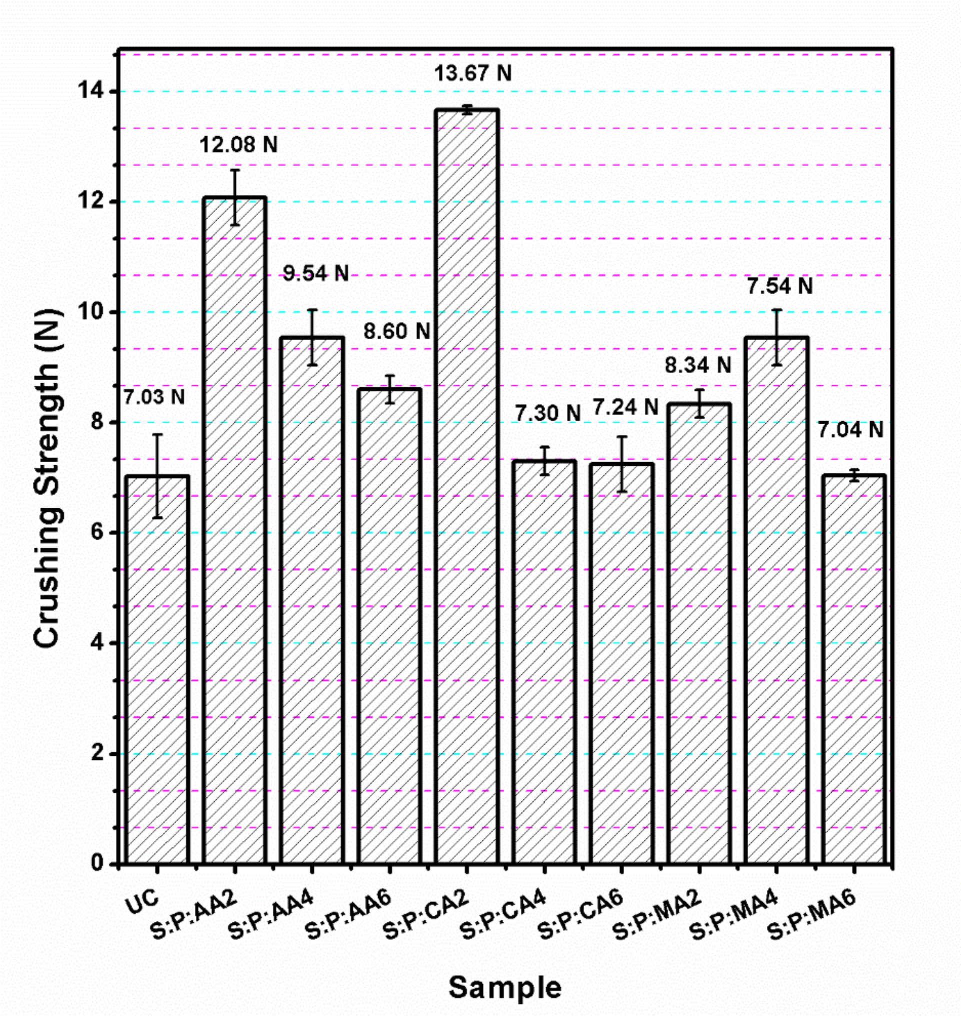


Figure 21: Crushing Strength comparison of Uncoated/Coated Urea

4.6 Efficiency:

The efficiencyof coated and uncoated urea samples was found at 9 min using equation (7). The best result was shown by S:P:AA2 wt.% and S:P:CA2 wt.%. This is shown in **Table 6** and **Figure 22.**

Table 6: Efficiency Values at 9 min of Coated/Uncoated Urea

Samples	% Efficiency at (9 min)
Uncoated Urea	0
S:P:AA2	70.1
S:P:AA4	9.0625
S:P:AA6	0
S:P:CA2	50.7375
S:P:CA4	14.275
S:P:CA6	0
S:P:MA2	5.825
S:P:MA4	3.6
S:P:MA6	1.875

Uncoated Urea sample released after 6 min due to a quick release of Nitrogen Content. Sample S:P:AA2 shows the highest efficiency of 70.1% whereas S:P:AA4 shows less efficiency at 9.0625 % with S:P:AA6 having 0% efficiency.

The efficiency of S:P:CA2 is 50.7375 which is moderate and is acceptable. With the increase in the percentage of the CA, efficiency starts decreasing in S:P:CA4. It decreases to 14.275 and reduces to 0% with a further increase of CA in S:P:CA6.

All combination of Malic acid showed very low efficiencies. S:P:MA2 shows the efficiency of 5.825% which decreases to S:P:MA4 3.6% to 1.875 for S:P:MA6.

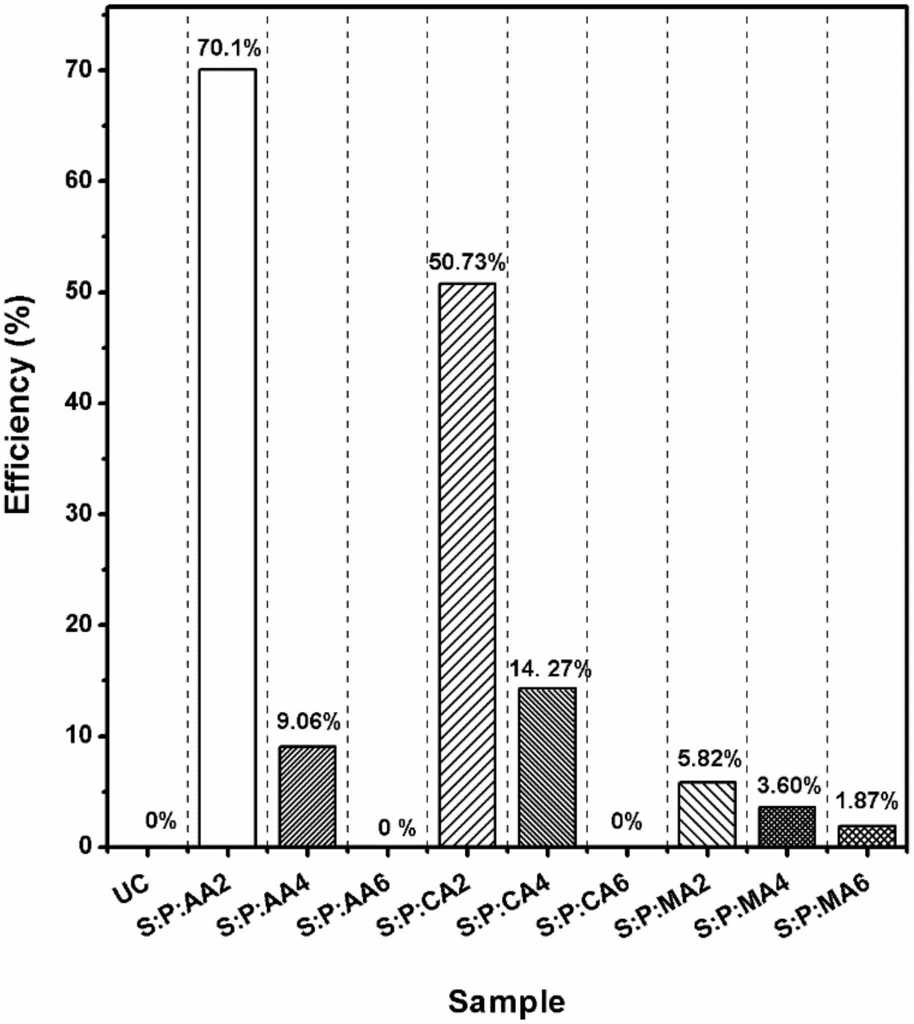


Figure 22: Efficieny of Uncoated/Coated Urea at 9 min

In **Figure 22** samples S:P:AA6 and S:P:CA6 has 0 efficiency values at 9 min due to their quick release before this time. But still, they retain longer then Uncoated Urea.

4.7 The release rate of Nitrogen:

The release mechanism starts when water vapourspenetrate through the coating. Vapourscondense and dissolve the fertilizer core due to an increase in internal osmotic pressure [63]. At this point, there exist two possibilities.

1) **Failure mechanism or catastrophic release:**

   Breakage of coating leads to release of entire prill content immediately. It is more frequent in inorganic type coatings like sulfur, which are brittle and fragile [64].

2) **Diffusion Mechanism:**

   If the coating resists the inside pressure, fertilizers could be released through diffusion either forced by mass flow driven by a pressure gradient, by concentration gradient across the coating or by the combination of these two phenomena. It is more characteristic of coatings like polyolefin, polyurethane and alkyl resin coatings. In diffusional release due to the gradual release of fertilizer sigmoidal shape is obtained when plotted [34].

The nutrient release mechanism is consist of 3 main steps by Shaviv (2001) [63]:

1. The initial stage of the lag period during which negligible release is observed.
2. The constant release stage, and
3. The last stage during which a gradual reduction in release rate occurs also called mature stage.

4.7.1 Release rate of Nitrogen from Uncoated Urea:

The release rate of Nitrogen from Uncoated Urea Prill was determined in water. Amount of Nitrogen release was examined as a function of time at 25 ºC. The release of Nitrogen from conventional uncoated fertilizer was very fast and all Nitrogen was released within 3 min. This is shown in **Figure 23**. This is an actual and usual trend of Nitrogen release from Nitrogenous fertilizers without any coating.

As there is no physical barrier to the fertilizer water dissolves it immediately. Here, we can say that catastrophic release can be seen. No gradual or lag period is demonstrated by fertilizer due to the absence of any physical barrier. Physical barrier acts as a coatingand prevents abrupt release causing diffusion to occur. Diffusion here will release fertilizer slowly through coating barrier.

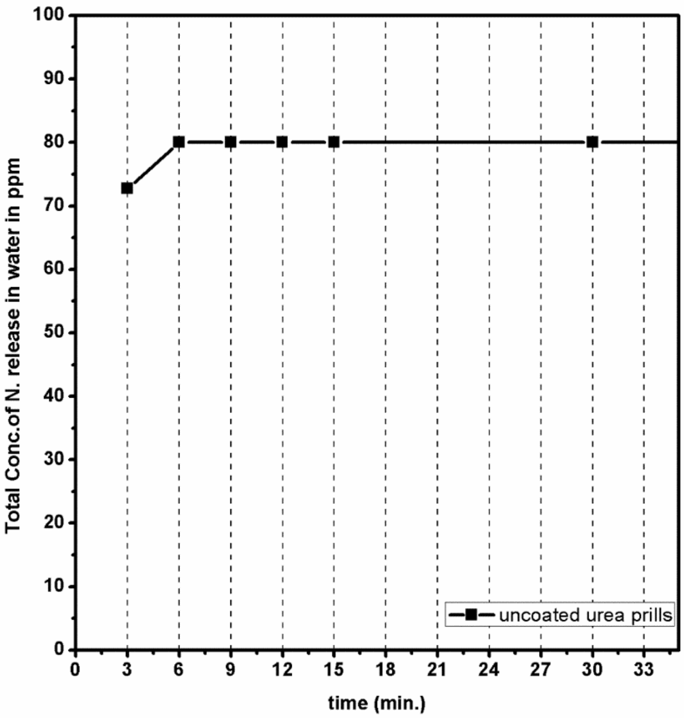


Figure 23: Release of total Nitrogen of uncoated urea prills

4.7.2 The release rate of Urea from S:P:AA2, S:P:AA4, S:P:AA6:

The sample in **Figure 24** contains Starch/PVA and Acrylic Acid 2 wt. %. All prepared samples reveal a slow release of Nitrogen from Urea Prills as compared to the uncoated urea prills in **Figure24**. In **Figure 24** the total Nitrogen release by diffusion. From 3 to 6min. the release could be lag stage release. From 6 to 9 and then to 12 is attributed as a gradual release. This is diffusional release in which the water penetrates through diffusion and nitrogen will release slowly from inside of the coating to the outer surface through diffusion[63]. From 12 min to onwards mature release could be seen. The water penetrates the fissures or damaged coating and develops high pressure with the gradual release of Nitrogen through polymeric coating[34]. At 12 min total Nitrogen in urea is released into the water. The urea prills along with the coating dissolve into the water and cannot be seen anymore with the naked eye.

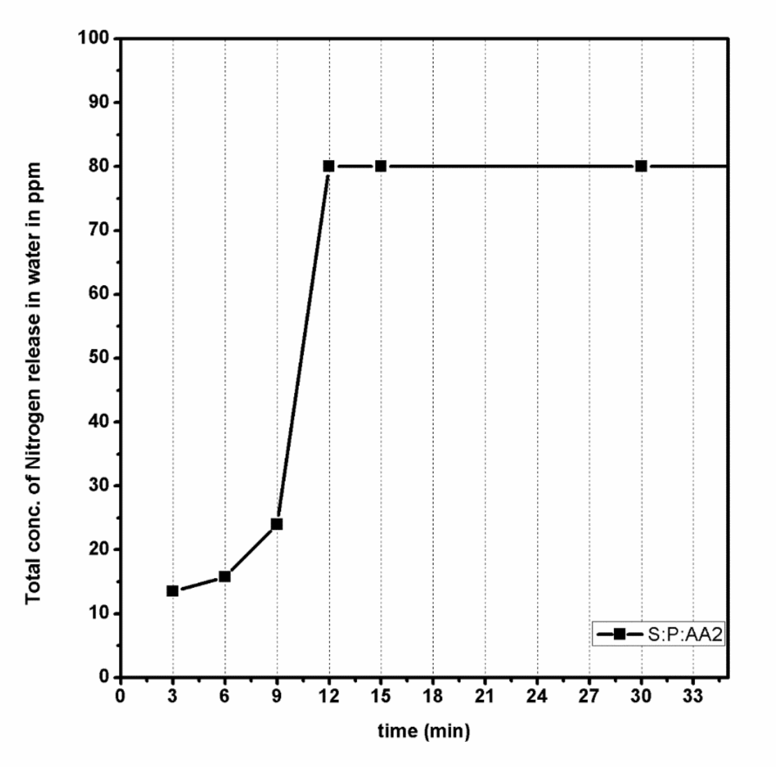


Figure 24: Nitrogen Release pattern of S:P:AA2 coated urea prills

The sample in **Figure25** contains Starch/PVA and Acrylic Acid 4 wt. %. In this sample, the total Nitrogen release also followed diffusion phenomena. In the start, we can see there is no lag stage. From 3 to 6 then to 9 and 12 it follows a gradual release rate. However, from 12 min to onwards the Nitrogen will release completely and dissolves in water. At this stage, the urea disappeared into the water along with the coating. This stage could be attributed toa mature stage. At this stage the release is constant. Here the diffusion release occurs but no catastrophic release has examined. Here the release concentration is higher than the 2 wt. % coating of acrylic acid shown in. In comparison with S:P:AA2, we can deduce that with the increase in the concentration of the plasticizer the release rate becomes more gradual. But the mature stage for both the samples starts at 12 min.

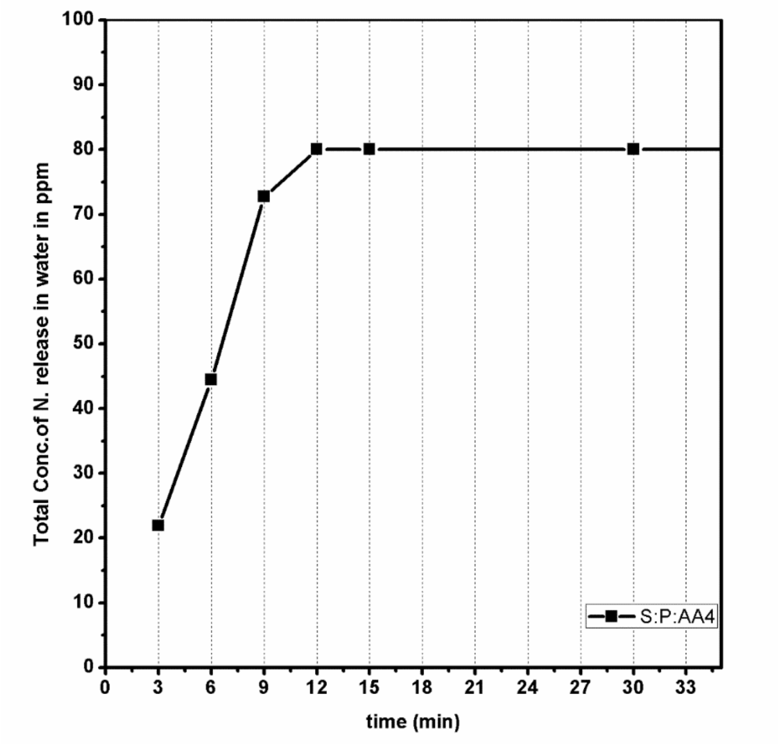


Figure 25: Nitrogen Release pattern of S:P:AA4 coated urea prills

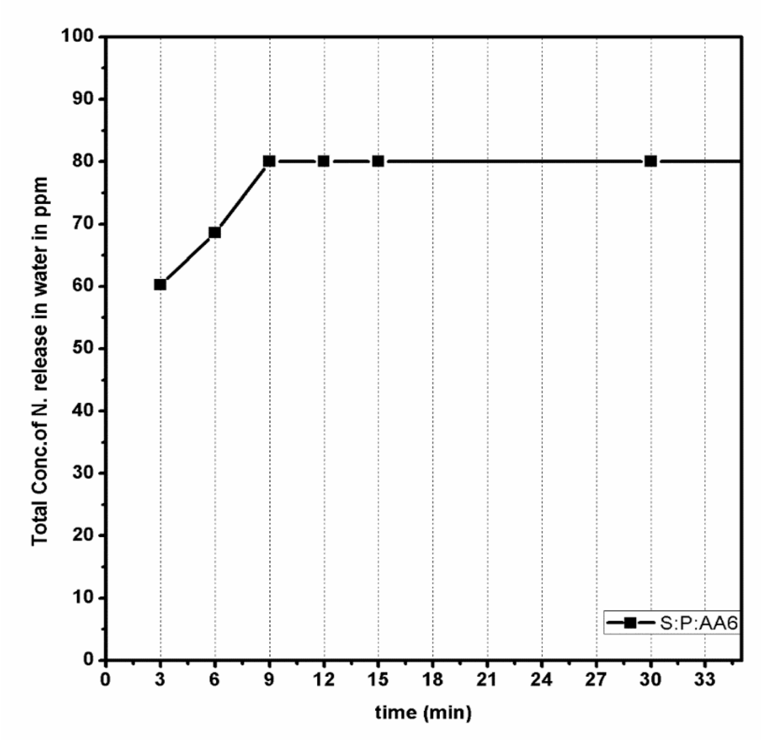


Figure 26: Nitrogen Release pattern of S:P:AA6 coated urea prills

The sample shown in **Figure 26** contains Starch/PVA and Acrylic Acid 6 wt. %. In this sample, there is no lag stage and we can assume that the release is gradual from 3 to 6 and then to 9min.At 9 min. the release becomes constant. This stage could be assumed to be a mature stage. The release concentration starts from higher than the previous of 4 wt. % acrylic acid. Again, the diffusional release can be seen here. After 9 min it disappears completely into the water. The reason may be due to the restriction in polymeric chains with more availability of the plasticizer. This will make the coating less flexible and fragile. So, this coating may be prone to cracking of the coating. These cracks lead to the early release of Fertilizer.

4.7.3 The release rate of Urea from S:P:CA2, S:P:CA4, S:P:CA6:

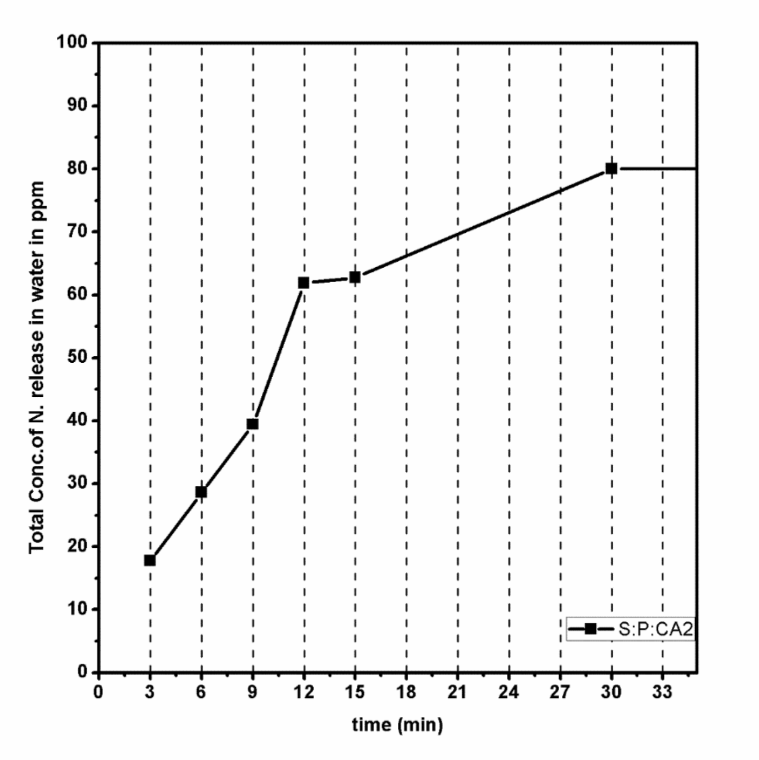


Figure 27: Nitrogen Release pattern of S:P:CA2 coated urea prills

The sample shown in **Figure 27** contains Starch/PVA and Citric Acid 2 wt. %. It follows the diffusion mechanism for release of Nitrogen. From 3 to 12 min it follows the gradual release. Then from 12 to 15 min, it could be a lag stage in which negligible release can be seen. Likewise, from 15 to 30min it again shows gradual release. Finally, after 30min mature stage of nitrogen release has reached.

This huge time lapse shows that this coating retards the release of Nitrogen from urea sample better than all previous coatings. This could be the verification of SEM, Crushing Strength, Efficiency results.

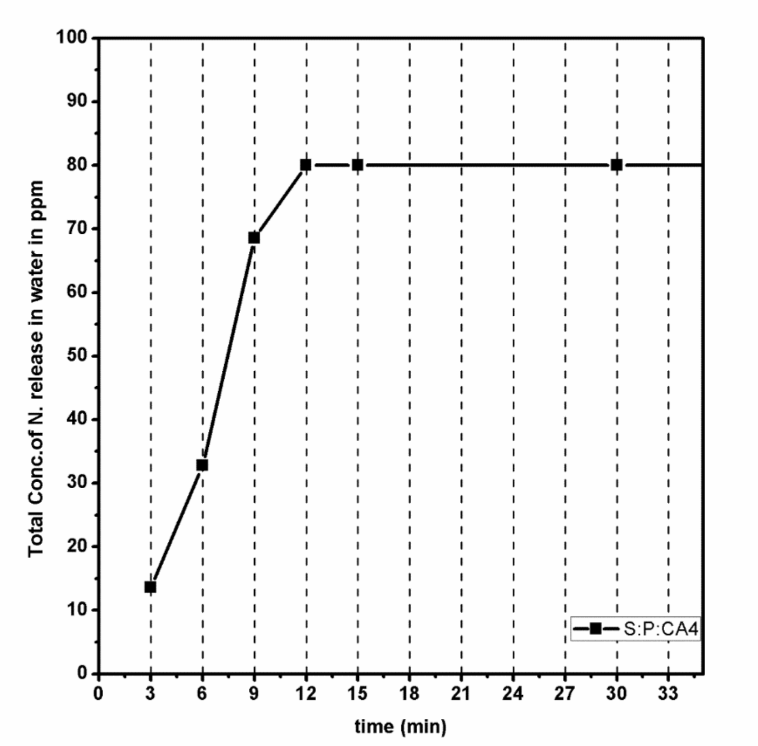


Figure 28: Nitrogen Release pattern of S:P:CA4 coated urea prills

Figure 28 shows S:P:CA 4 wt.% results. It can be seen from the graph that 3 to 12 min is the gradual release of fertilizer. From 12 to 15 min could be attributed to the lag period or here may be the mature stage has started. Then after 15 minutes the release rate and pattern are constant. The best and slow release rate is achieved for this sample. At this time, it completely dissolves in water along with the coating and cannot be seen with the naked eye.

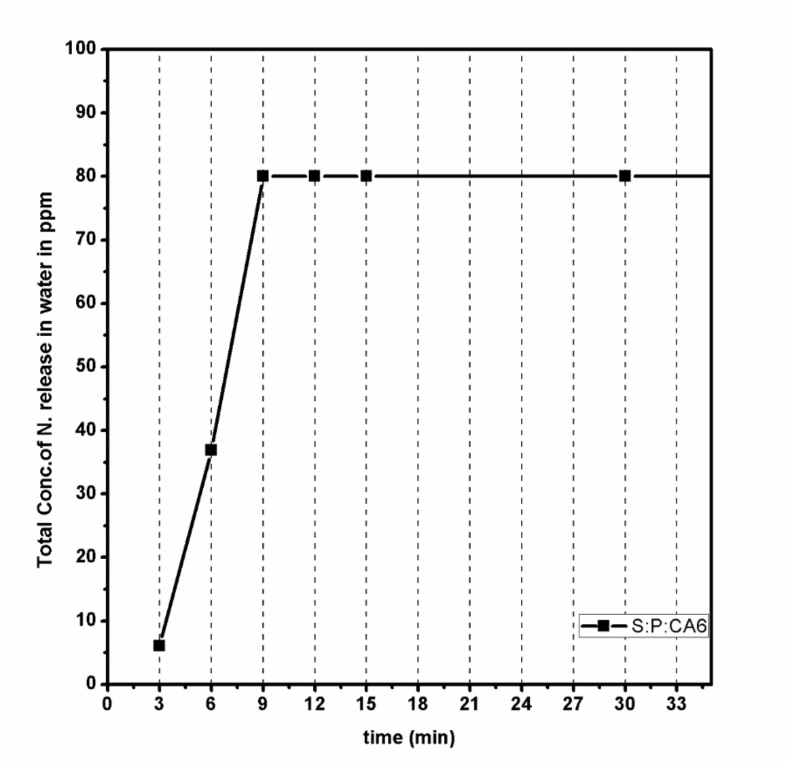


Figure 29: Release pattern of S:P:CA6 coated urea prills

The sample in **Figure 29** contains Starch/PVA and Citric Acid 6 wt.%. It releases nitrogen from 3 to 6 min and then to 9 min and then becomes constant. It may be assumed here that the release is not gradual. It could be a failure or catastrophic release. Due to the high difference in the release rate from 3 to 9 min. It is difficult to attribute this release as diffusion release. After 9 min mature stage starts. At 9 min it dissolves completely into the water and cannot be seen with the naked eye at this point.

4.7.4 The release rate of Urea from S:P:MA2, S:P:MA4, S:P:MA6:

The sample in **Figure 30** contains Starch/PVA and Malic Acid 2 wt.%. The figure is representing the diffusional release of the nitrogen from the coating. It increases gradually from 3 to 6 and then to 9 min. But from 9 min to 12 min a slightly increases. At 12 mature stage release has reached. **Figure30** contains starch/PVA and Malic Acid 4 wt.% It starts at a very low value near to the lag stage that is initial where release is almost 0. It also follows the diffusionrelease, but the initial increase gap is quite large than any other coatings. It continues to increase like this up to 9 min. From 9 min onwards, it slightly increases to12 min. After 12 min mature stage has reached. So, the release from the coating becomes constant.**Figure30** indicates the graph of Starch/PVA and Malic Acid 6 wt. % and completely releases Nitrogen at 12 min.

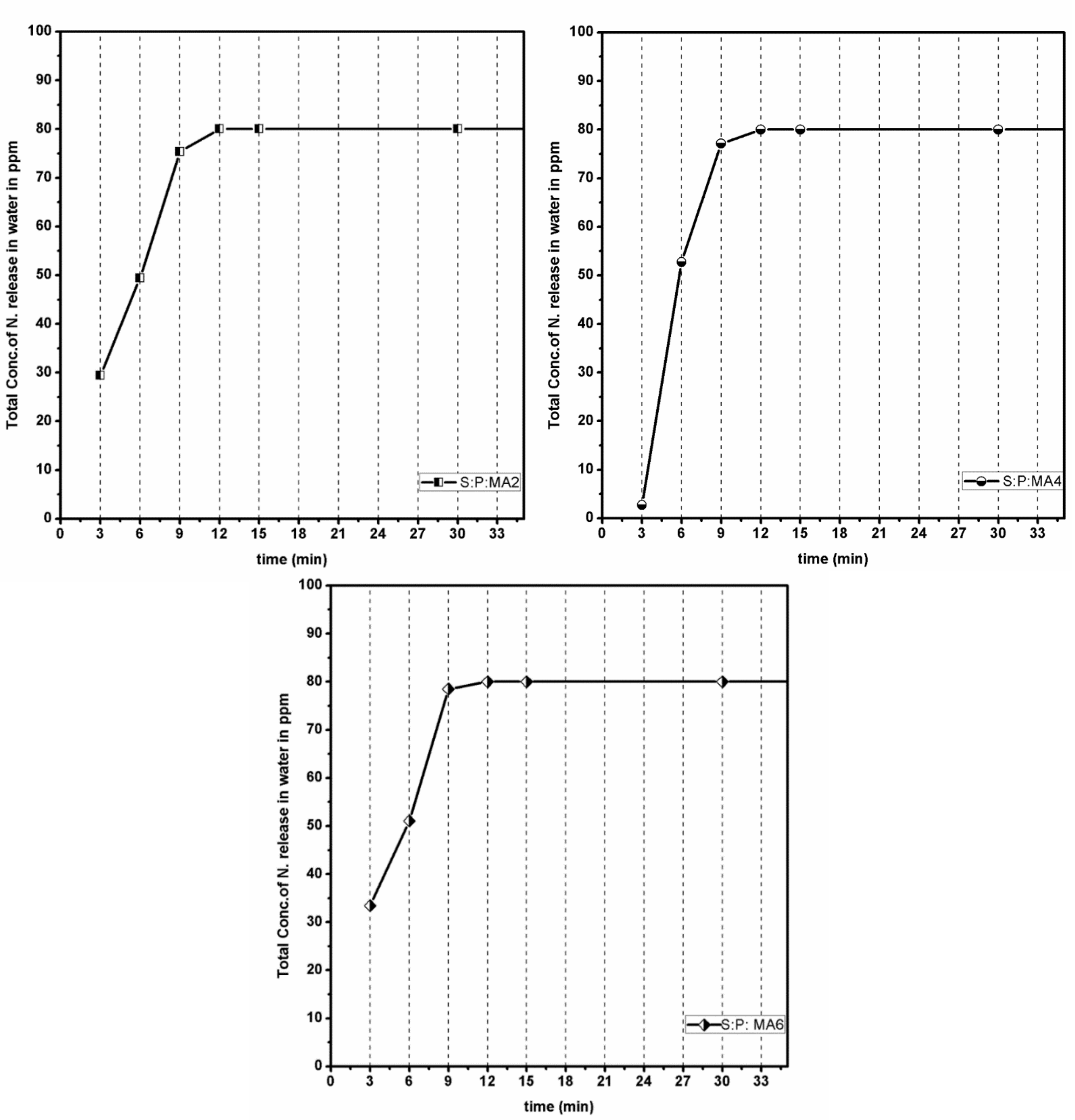


Figure 30: Release Pattern of Starch/PVA/Malic acid coated urea prills

This also follows the diffusional release with 3 to 6 and 9 min attributed to gradual release. From9 to 12 min and then to 15 min could be assigned as a lag stage because the change could be negligible here. After 15 min the mature stage could be seen. From all these combinations with MA, S:P:MA4 showed good results with the lowest release of fertilizers. These results are verification of SEM, Crushing Strength and Efficiency analysis.

Conclusion

The coating of urea was done to minimize nitrogen loss through volatilization, leaching and denitrification. Due to leaching, surface runoff and denitrification the plant takes up of urea and utilization efficiency is generally less than 50 %. It increases the fertilization expenditure per season and reduces crop productivity. Such problems can be addressed by modifying conventional fertilizers with the controlled release fertilizers. These fertilizers inhibit this loss and serve the nitrogen with the metabolic requirements of the plants. Many sealants, binders, plasticizers and protective agents have therefore been used to tackle the immediate burst effect. This study showed that malic acid, citric acid and acrylic acid can affect the sealing properties of starch and PVA in making conventional urea into control release urea fertilizer. At constant weight concentration citric acid and acrylic acid showed good barrier properties as compared to malic acid. Citric acid 2 wt. % and acrylic acid 2 wt. % showed best in terms of lowest release rate. Malic acid 4 wt. % also has shown good results. All other formulations gave satisfactory results but better than conventional urea fertilizer. XRD patterns showed highly sharp peaks in many of the combinations. This showed crystalline coating along with some amorphous regions. FTIR confirms formation of ester linkages between starch, PVA and plasticizers. It also indicated the characteristic peak of carboxylic acid. Starch/PVA/Citric acid 2wt. % has shown the best crushing strength and slowest release rate among all the combinations. Starch/PVA/Acrylic acid 2wt. % has also shown better results. It can be concluded from the above results and observation that acrylic acid has performed very well as compared to malic acid; however, citric acid is the best option.

Future Recommendations

In the review of the present research following recommendations are advised to further improve and explore the best coating and percentages for encapsulation of urea.

- Release Kinetics can also be applied to these formulations.
- Cost analysis can be done to analyze the efficiency increase.
- Instead of prills, urea granules can also be used.

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