To study the effect of PVA/Starch blends on dissolution rate of slow release urea fertilizer

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Dedicated to my ***Family***

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Abstract

The earth's population is increasing every day which cause a rise in global food requirements. To overcome this problem of global food security, farmers are bound to employ the fertilizers for agricultural needs as well as to minimize the environmental pollution hazard in the form of various emissions to atmosphere. The most important nitrogenous fertilizer that is extensively used in crop growing due to its sky-scraping nitrogen content composition (46%) is urea. Nevertheless it was found that up to 70 per cent of the common urea application is lost to the atmosphere that resulted in significant contamination to atmosphere and escalating expenditure.

The efficiency of urea can be enhanced by reducing its dissolution rate. This MS research work will focus on use of PVA and Starch with Molasses, Plaster of Paris and Sulphur as a coating material.

Slow release urea samples were prepared by using Dip Coating Technique. Various formulations of different coating materials were made and their dissolution rates were determined by using most useful analytical technique. Conductivity meter method was used to calculate the dissolution rates of slow release urea. Surface Topography was founded by using (SEM). XRD was used to find crystallinty. FTIR was used to find Functional Group. EDS was used for Elemental Analysis. Moreover Crushing Strength and Moisture Contents were also found. Cost Estimation was also done.

This technology gained importance in recent years to produce slow release urea fertilizer by using efficient methods with cheap materials. These materials not only increased the efficiency of fertilizer in terms of reduction in dissolution rate of urea fertilizer but also acted as multi-functional fertilizers or compound fertilizers.

Keywords: Slow release urea fertilizer (SRUF), Dissolution rate, Starch, PVA, Sulphur, Molasses and Plaster of Paris

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Abbreviations

Plaster Of Paris (POP)

Slow Release Urea Fertilizer (SRUF)

Poly Vinyl Alcohol (PVA)

Scanning Electron Microscopy (SEM)

Universal Tensile Machine (UTM)

XRay Diffraction (XRD)

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Chapter 1 : Introduction

Nitrogen is the main constituent of fertilizer that makes possibility of intensive food production. A variety of wastes and theirs decomposition products as well as ammonium sulphate as a by-product from coal coking were the basic sources of nitrogen for growth of plants before synthetic fertilizers. All of those types were messy and insufficient to meet the needs [1]. Currently Urea (46%N) is the larger source of nitrogen as a fertilizer in US due to its higher nitrogen contents, ease of handling and low cost [2]. One of the most important fertilizers that is majorly used for crops growing is urea. It is found that up to 70 % of the urea is wasted that causes environmental pollution and also makes the crop cultivation expensive. This lose is due to leaching and volatilization of urea through soil. There are also some other losses of urea during handling and storage [3].

As earth's population has been increasing exponentially which is approximately 7.0 billion [4]. This figure will be around 9.5 billion by 2050 that will cause a rise in global food demand and it will be almost double per capita by 2050 [5]. The shortage of agricultural land in most of Arab countries is due to industrialization and land degradation from flooding problems [6]To overcome the problem of food shortage we are bound to use efficient fertilizers to meet agricultural needs as well as to minimize the environmental pollution hazards in different forms of various emissions [7].

Use of uncoated urea has drawbacks related to environmental pollution as well as economic factors that have a focal point of worldwide concern [8]. Urea efficiency is being enhanced by reducing its dissolution rate and this is being achieved by different techniques [9].

There are minimum 16 nutrients which are necessary for plant growth and completion of their life cycle. These nutrients are divided in to 3 non-mineral nutrients (C, H, and O) and 13 mineral nutrients. The source of non-mineral nutrients is normally water and air.

But the minerals are further sub divided into primary nutrients , secondary nutrients and micro- nutrients as shown in fig – 1 [10].

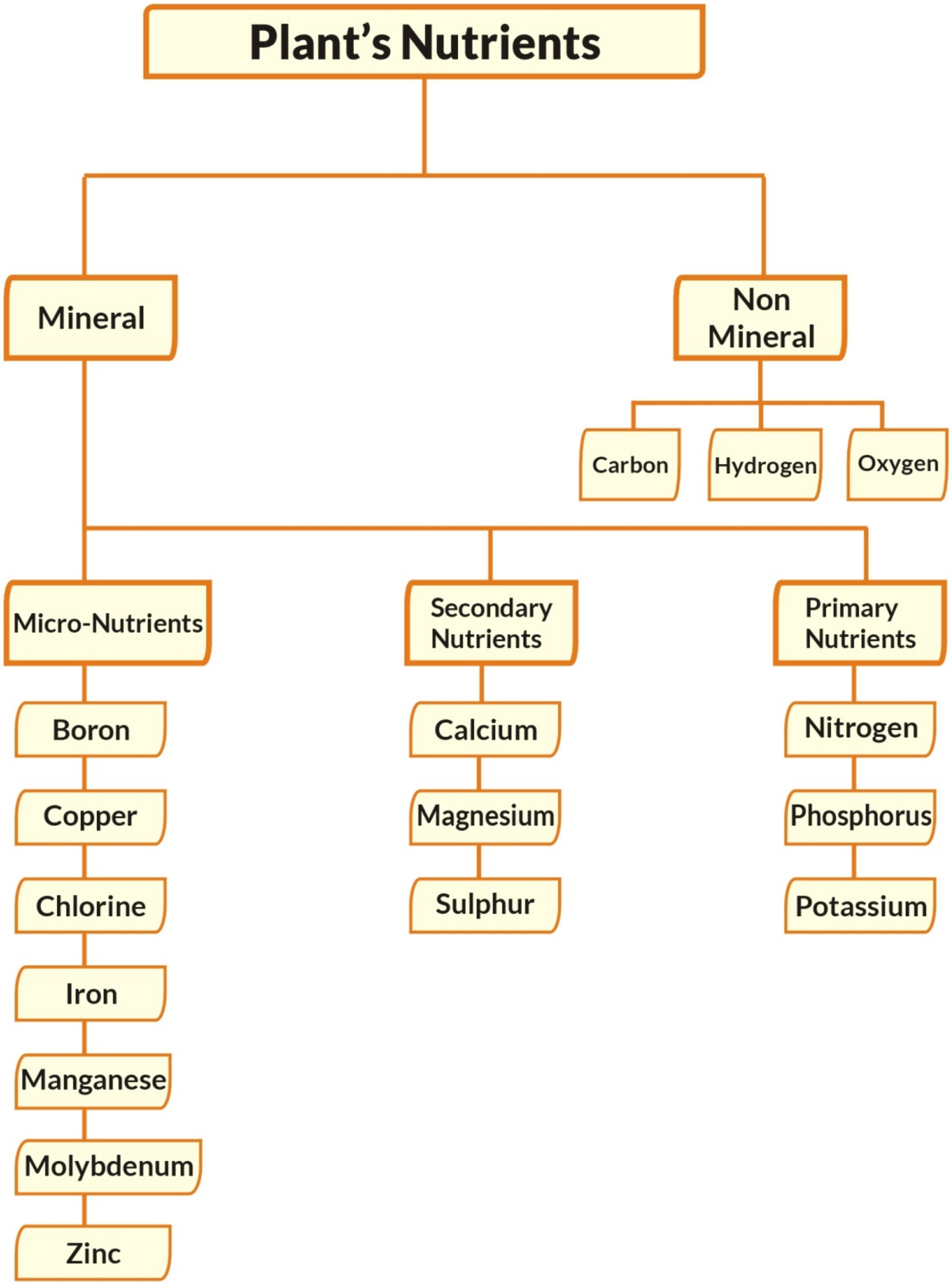

Figure 1 : Classification of Plant Nutrients [12]

Roots and leaves of plants absorb the essential nutrients in different forms. These nutrients are present in handsome amount in the soil but a limited amount of these nutrients is normally available for plants. The factors include soil pH, soil colloids interactions and physical condition of soil such as compaction, aeration temperature and moisture contents. Essential nutrients are present in all physical states (i.e. solid, liquid and gas) in soil [4]. Essential nutrients and their different forms are given in Table 1

Table 1: Essential plant Nutrients and their different available forms

Essential nutrients	Available form
Non-Mineral nutrients	
Carbon	CO_2 (g)
Hydrogen	H_2O (l) and H^+
Oxygen	H_2O (l) andO_2
Mineral nutrients	
Major nutrients	
Nitrogen	NH_4^+ and NO_3^-
Phosphorus	HPO_4^- and $H_2PO_4^-$
Potassium	K^+
Secondary nutrients	
Calcium	Ca^{2+}
Magnesium	Mg^{2+}
Sulphur	SO_4^{2-}
Micro- nutrients	
Iron	Fe^{2+} and Fe^{3+}
Manganese	Mn^{2+}
Zinc	Zn^{2+}
Copper	Cu^{2+}
Boron	$B(OH)_3$ (Boric Acid)
Molybdenum	MoO_4^{2-}
Chlorine	Cl^-

1.1 Background

The population has been increased about 7.0 billion [4] and will be reached 9.5 billion by 2050. Food need per capita will also be increased and it will be doubled in near future[6] The reduction in agricultural land is also one of the main factors towards food shortage. It is due to modern urbanization, industrialization, high flooding rate and dehydrated soils. To meet demand and supply chain of global food, yield of food crops must be increased. Crop yield depends upon many factors like nature of land, pH of soil, environmental conditions, irrigation water and way of use of fertilizers. Most important factor is the use of conventional urea fertilizer for moderate plant growth. High prices and low utilization of urea fertilizer causes the lowering of yield of crops [7]. It results into NO_x emissions that cause unwanted environmental impacts which can be explained by nitrogen cycle as follows:

1.2 Nitrogen Cycle:

Nitrogen cycle is based on circulation of nitrogen in close loop in earth's atmosphere. It is found as most abundant element and essential for all living entities. But its availability is limited due its form. It is found as diatomic form (N_2) instead of elemental form (N).Bond breaking between two nitrogen atoms is very difficult to make it reactive and useful for living entities. Production of nitrogen (N) as a fertilizer not only makes it reactive but also increases the agricultural yields [11]. The use of urea has been increased by 20 times during 1950-2000 [12]. The reactive nitrogen in urea increases its efficiency but it also has adverse effects like its dissipation through aquatic, atmospheric and earth eco systems. This dissipation causes atmospheric changes and adverse effects on human health and other living entities [13]. Emissions of greenhouse gases generated by agricultural activities are 10% [14] and there are about 60% of it is due to reactive N applied to soil as N_2O emissions [15].

1.3 Nitrogen Losses through soil:

When urea is through to soil, two type of losses are observed as follows

1. Permanent Losses
2. Temporary Losses

1.3.1 Permanent Losses:

- i. De-nitrification (conversion of NO_3- to N_2 gas).
- ii. Leaching (transfer of NO_3- to the soil).
- iii. NH_3 volatilization (from soil and plants).
- iv. Removal and plant uptake in harvested portions of the crops.

1.3.2 Temporary Losses:

- i. Curb (uptake by micro-organisms)
- ii. Interchange (binding to soil particles and vice versa)

Note: As N is present in Soil and is available for Plant that's why these are referred as temporary losses

Cycle of Nitrogen is shown in Fig 2:

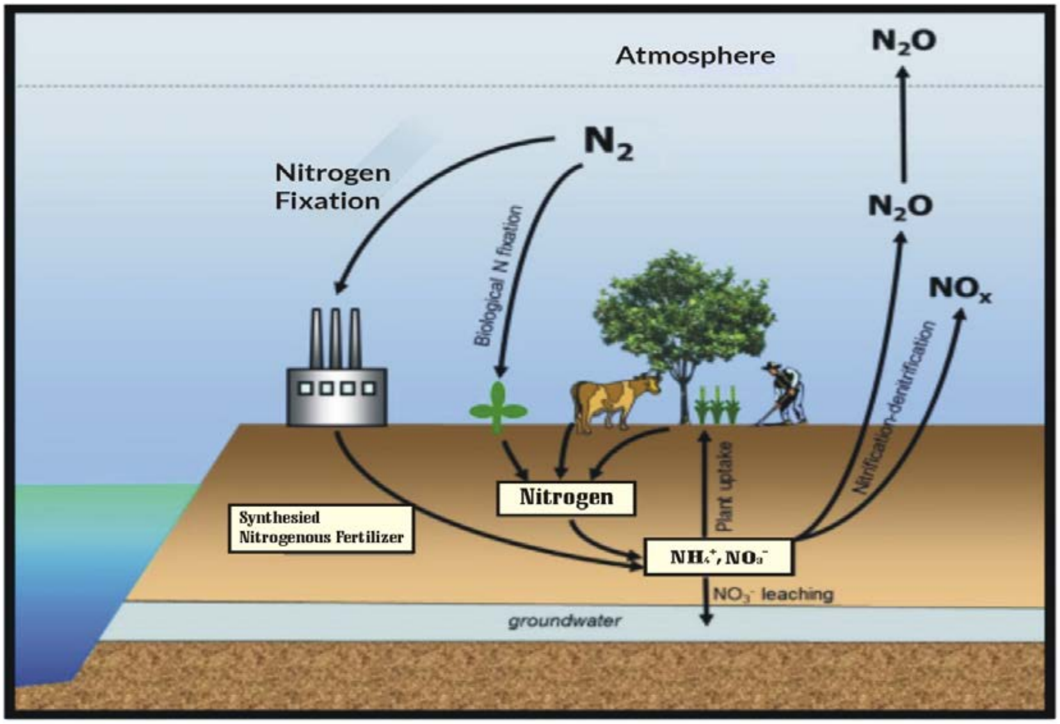

Figure 2 : Cycle of Nitrogen [16]

These losses increase the greenhouse gases emission as well as are responsible for water pollution [16]. The ultimate solution of this problem is to produce slow release urea which increases not only the efficiency of urea but also reduces the environmental pollution which is caused by the conventional urea [3].

1.4 Slow Release Urea Fertilizer (SRUF):

Slow release urea fertilizer was produced to provide essential nutrients to plant at slow rate according to plant requirement and beneficial to increase crop production [3]. A slow release urea is one of the fertilizer that is coated with the natural and plant essential molecules those provide the nutrients to plant, according to plant needs [17].

1.4.1 Functioning of Slow release Urea Fertilizer (SRUF):

The functioning of slow release urea is a complicated scheme because it is dependent on many factors such as soil condition, soil type and different types of coatings etc. Method for functioning of coated fertilizer was found in literature called as multi-stage diffusion model [18].

1.4.2 Multi-stage Diffusion Model:

This model consists of following steps:

a) Water diffuses into core of the coated urea.
b) Core inflammation and osmotic pressure build up inside the core.
c) Controlled release of core through coating film.

According to this model in 1st step, water diffuses inside the coated urea granule core. In 2nd step, this water inflammated the granule core and builds up osmotic pressure inside the core. In last step the inflammated core results into the diffusion of nutrition's through coating which acts as a membrane to provide the slow release of urea according to plant requirement as shown in figure 3.

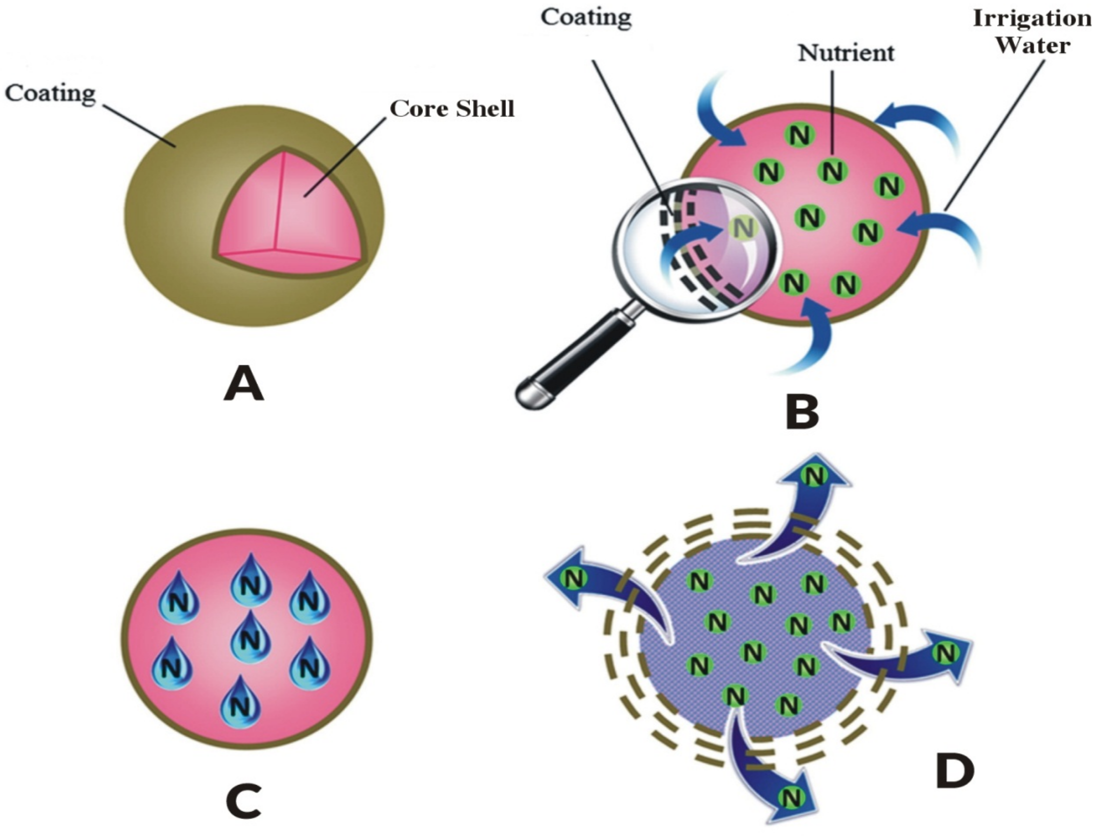

Figure 3: Multi-Stage Diffusion Model [19]

1.4.3 Advantages of Slow Release Urea Fertilizer (SRUF):

Slow release urea fertilizer (SRUF's) is cheap in the sense of its high efficiency as compare to uncoated urea, which reduces its quantity and ultimately labour application cost is also reduced as compare to uncoated urea. It also enhances the nutrient utilization by the plants and reduces the seed toxicity by slow nitrogen diffusion rate that damages the seed in case of uncoated urea. It prevents the dermal infection, burning of leaves and problems of inhaling emissions after its application to the soil. SRUF improves the handling properties of urea, vegetation rate of seeds and quality of soil in terms of its fertility that increases the crop yield [19]. The increase in efficiency of urea can be obtained by reducing the dissolution rate of urea. It is obtained by coating the urea with different materials.

1.4.4 Limitations of Slow Release Urea Fertilizer (SRUF):

Development of Slow Release Urea Fertilizer (SRUF) has been considered as a burning issue from decades [17]. Slow Release Urea Fertilizer (SRUF) is facing marketing acceptance issues as compare to the common urea. Many coating materials are non-biodegradable, so they are creating environmental pollution in soil as well as in atmosphere. In soil they cause toxicity that reduces the seed growth rate and resulted into a lower crop yield. Some Slow Release Urea Fertilizers (SRUF's) change the soil pH in a harsh manner which is undesirable in many food plants. Pre mature release of nutrients has been observed due to the abrasion of urea granules [20]. The most important factor for adaptation of Slow Release Urea Fertilizers (SRUF's) is its release kinetics in the soil. It is mainly due to the various soil types on the basis of pH, bioactivity of soils, moisture contents and wetting-drying cycles of soil [13].

Chapter 2: Literature Review

Slow Release Urea Fertilizer (SRUF) history started from early 1960's according to the literature review. This journey was followed by the use of different materials based on their ability not only to increase the urea efficiency in terms of its release rate but also to provide secondary nutrients to the plants.

2.1 Classification of Materials used for the coating of urea:

Materials used for the coating of urea are classified as follows.

2.1.1 Organic Compounds:

Natural and organic compounds are those compounds that include carbon, hydrogen and oxygen as predominant components. Natural compounds are then categorise to naturally available compounds (dung, sewage wastage) and synthetically made nitrogen. The said compounds are sub divided to decomposing compounds, like Urea formaldehyde and chemically decomposing compounds like isobutyledene-diurea (IBDU) [16].

Isobutyledene diurea (IBDU):

Ito [22] worked to produce double coated urea in 2005, which consisted inside layer of ineffectively solvent iso butyliden diurea and outside layer of starch mixed with wax in a granulator blender for mixing. The discharge rate was changed by conforming the thickness of both inside and outside coatings by using HPLC. It was observed that by using single coating material a control release mechanism occurred. But a better controlled release pattern was observed in dual layer coating procedure. This pattern consisted of two stages, in 1st stage slow release of nutrients and in the 2nd stage increase in release rate was observed. In this pattern, the nutrient's core was shrunk when granules were immersed in water due to dissolution process. In 2nd stage, equilibrium was established because of the concentration of nutrients in core started decreasing inside the core. Single layer produced higher diffusion rate of soluble particles as this layer provides micro paths. These micro paths resulted into faster nutrient release. Second layer contained polyethylene glycol and starch coating which was sprayed from the top of fluidized bed coater. Reduced release rate was found by the increase in concentration of starch in coating solution.

Green natural rubber-g-modified starch:

Starch was used by Riyajan in 2012. Starch was made by gelatinizing it with water at 80^{o}C. Then cooled and mixed it with $K_2S_2O_8$ for 45 min at a temperature of 60^{o}C.

Teric®16A16 was also used with starch by polymerization method. In this method natural rubber was used and continuous stirring was carried at 60^{o}C for about 3hours. SRUF was made by dip coating of the urea with the polymer and then dried at room temperature. UV-vis spectrophotometer was used for finding the dissolution rate of coated urea. After diffusion mechanism the core's shell was left in which core was made of NR which was hydrophobic in nature while shell was made up of starch. Starch is hydrophilic in nature due to the presence of hydroxyl functional group [20]. Different additives were studied to convert starch into hydrophobic in nature but it was found by doing this it increases the cost of urea which is undesirable due to the commercialization of the process.

Lignin:

Lignin is a naturally occurring compound that is available from paper and pulp industry in the form of waste [23]. In 2008, Perez used lignin and urea to produce coated urea and the mixture was dipped in an oil bath of silicon made. This mixture was heated and then cooled at room temperature to get a glass like material which was grinded to obtain the required size in a crusher. The formulated particles act as SRUF. This study was further carried out with ethyl cellulose. Urea coating was carried out in fluidized bed equipment. EC showed good physical as well as chemical properties. It is also nontoxic in nature. In this method 5% ethanol solution of ethyl cellulose was prepared and showered to the urea in spray coater at 60^{o}C. Drying was done by hot air at 70^{o}C. Coating thickness was changed to produce different samples and then those samples were subjected for analysis. Lignin and EC based coated urea was analysed by using leaching method. Dissolution rate was observed in three stages as very slow, constant and decay release. But results showed that Lignin was failed to reduce dissolution rate as compared to ethyl cellulose due to uniform coating. However ethyl cellulose coated granules showed better results but the thickness of coating produced had inverse effects on controlled release process. The complexity of the process was a main problem for its commercialization.

In 2011, Mulder [24] used Bio plast (Soda Flax Lignin) with a plasticizer acronal and alkyl succinic anhydride (ASA) to produce SRF. Rotary pan coater was used in which 25% Bioplast; plasticizer and alkyl succinic anhydride (ASA) were sprayed to urea granules. The temperature was set at 70 ^{o}C and released rate was determined by refractive index method. For slow dissolution rate and uniform coating, the coating solution was sprayed in three stages. In 1st stage, a large quantity of coating solution was sprayed which encased the urea granules in order to suppress the nutrient release from urea granules. To fill the micro pores relatively small amount of coating solution sprayed for the uniformity of coating material. ASA played an important role due to hydrophobic nature and helped to reduce the dissolution rate. Coating materials adhered the granules due to cross-linking of plasticizer for2 weeks but it was failed to produce further reduction in dissolution rate. It was not able to meet the market standards. Further research realized that to increase efficiency of coated urea in terms of dissolution rate, cellulose could be modified chemically..

Ethyl Cellulose and Cellulose acetate phthalate:

Lu [27] produced coated urea by using 5% acetone solution at 30 ^{o}C along with ethyl cellulose and cellulose acetate phthalate. Wurster fluidized bed coater was used for coating purpose. The temperature range was from 32 to 51^{o}C. Conductivity experiment was carried out to find dissolution rate of both coating solutions. High release rate was found in the case of ethyl cellulose as compared to cellulose acetate phthalate. Three staged release mechanism showed initially high release rate then constant and at last slow release rate.

2.1.2 Polymer Compounds:

Major category in (SRF's) is polymeric coated urea fertilizers that have better release rate of nutrient. These are classified as thermoplastics (Rubbers) and resins (Zeolites). These are normally applied on surface of urea granules and maintain a controlled release rate. These coating materials can be hydrophobic in nature like polyolefin and rubber. Hydro gels can also be used as coating materials for producing SRUF.

Polyurethane:

SRUF was prepared by using polyurethane as a coating material [32]. Rotary drum coater was used to for coating purpose in which a coating mixture containing Isocyanate, wax and polyols were added to urea granules. Isocyanate and polyols resulted into a thick coating layer of polyurethane on urea granules and wax gave the binding strength. A significant reduction in dissolution rate was found after 50 days of soil testing experiments.

Thermocol:

Yang used Waste polystyrene (thermocol) along with wax and polyurethane as a coating binding material [33]. Coating mixture was prepared in an agitator and was employed to urea granules in a spray coater and then an oven was used to remove the excess solvent. Measurement of Release rate was done by Kjeldahl method. By Increasing the wax quantity did not show any significant improvement in release rate where as high amount of polyurethane worked well.

2.1.3 Inorganic compounds:

Sulphur:

Sulphur is the oldest coating material for producing SRF and has more than five decade’s history. The Tennessee Valley Authority (TVA) of USA made Sulphur coated urea in early 60’s. Blouin coated the urea granules with sulphur and petrolatum as a binding material [17]. Polymers were used to enhance quality of sulphur coated urea [35]. Liu [18]used dicyclopentadiene along with sulphur as a coating material to reduce its dissolution rate. Gullett et al [36]used a clay type material known as attapulgite with sulphur to form SRUF.

Gypsum:

It is a mineral composed of $CaSO_4.2H_2O$. Gypsum is also famous as plaster of Paris. It can be applied as a coating material to improve the efficiency of urea. To close cracks paraffin wax was used on outer surface of urea to reduce the release rate of urea fertilizer [37].

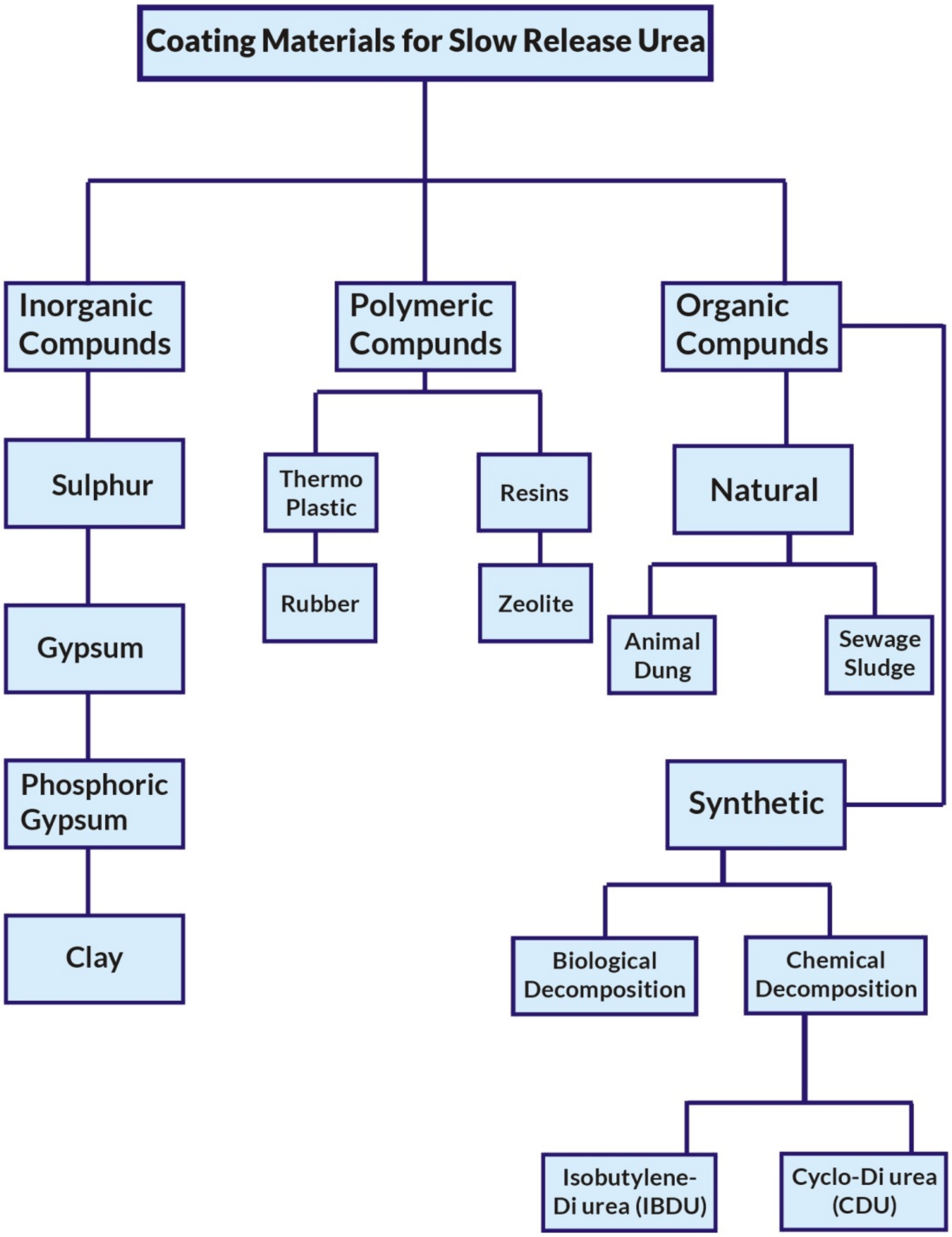

Figure 4: Classification of Coating Materials Slow Release Urea Fertilizer [32]

Chapter 3: Aim of Project

A Fertilizer is a very essential substance for the enhancement of soil fertility. Urea is the most important synthetic fertilizer that mainly contains nitrogenous contents. After its application, most of the urea is lost due to its volatilization. As a result not increases its cost but also increases the environmental pollution. Pakistan is an agricultural country and is larger consumer of urea fertilizer to increase the yield of crops. So it is essential to develop some new slow release urea fertilizer that could help to reduce the cost and toxic emissions.

3.1Objectives:

- Development of PVA/Starch coating on urea fertilizer.
- Characterization of uncoated and coated urea fertilizer
- To measure the effectiveness of polymeric coating material in termsof dissolution rate.

Chapter 4: Materials and Methods

This chapter focuses on the coating materials, method of its preparation and technique used for the production of slow release urea.

4.1 Materials

The materials that are used for preparation of novel slow release urea are granular urea (sieving was done to obtain uniform 4mm diameter of commercial grade Granular Urea obtained from Fauji Fertilizer Company Pvt. Ltd), sulphur (Dae Jung Korea), plaster of Paris or gypsum (Dae Jung Korea), Molasses (from Fatima Sugar Mills), starch (Dae Jung Korea) and Poly Vinyl Alcohol (Dae Jung Korea). Granular urea contains 46% N contents. Demineralizes water was utilized for making of coating solution. All materials were utilized without any additional treatment.

4.2 Coating Technique:

Coated urea fertilizer was produced by dip coating technique.

4.3 Sample Preparation:

Coating solution with different compositions as shown in Table4-1 was prepared with same methodology as follows. Pour 75 ml distilled water in 250ml beaker and placed it on hot plate preheated at 80 ^{o}C with stirring. After this, 5 gm of Polyvinyl Alcohol added in heated distilled water.10 gm starch, 5 gm sulphur and 2gm Plaster of Paris were also added in it with continuous stirring. Continuous stirring was done at 80 ^{o}C for 2 hours. When coating solution was prepared, cooling was done. Now, the pre-sieved urea granules were weighed and coated with solution by dipping in the solution using tweezers. It was very important to keep the dipping time constant for whole dipping process. After coating, coated granules were dried at room temperature.

Table 2: The composition of coating materials, water and binder

Sample	PVA	Starch	Sulphur	POP	Molasses	Water
1	6	10	5	2	-	77
2	5	10	5	2	-	78
3	4	10	5	2	-	79
4	3	10	5	2	-	80
5	6	10	5	-	2	77
6	5	10	5	-	2	78
7	4	10	5	-	2	79
8	3	10	5	-	2	80

4.4 Scanning Electron Microscopy:

To analyze structure and morphology of membrane at nanometers level Scanning electron microscopy is needed. High energy electrons are bombarded on the surface of material. SEM is used to determine the surface and cross section of membranes. Membranes were coated with gold and analyzed at 10 mm distance and with current of 90 mA.

Scanning electron microscope (SEM) is used to analyze the structure and morphology of membranes. High energy electrons are focused on the surface of the material. The analysis is performed to determine the surface and cross sectional morphology. Membranes were prepared by sputter coating of gold and analyzed at 10mm distance and 90mA current in SEM.

Components of SEM

SEM has following components

I. Display
II. Vacuum system
III. Detector
IV. Scanning system
V. Electron column
VI. Electronic control

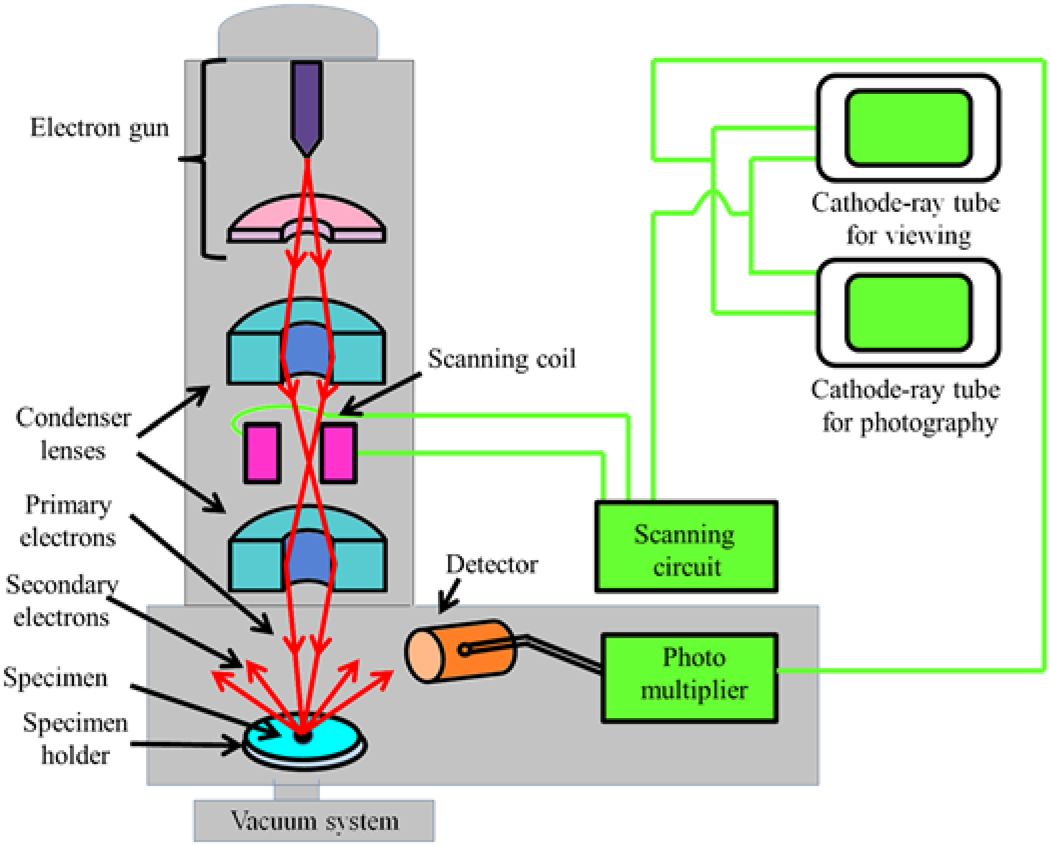

Figure 5: Schematics of scanning electron Microscope[33]

Working principle

High energy electrons are focused on the surface of material. For image of material secondary electrons are used while backscattered electrons are used for phase determination. The secondary electrons show the morphology and topology of membrane material. SEM is usually nondestructive technique because at lower magnification sample does not damage.

Magnification in SEM:

SEM uses electrons to show the image instead of optics. By tuning the length of scan (L_{spec}) on material we can adjust magnification. Calibration is important for every equipment and for SEM calibration is necessary. Length of scan of monitor is constant (L_{mon}), and thus linear magnification can be determined from the following formula:

$$M = \frac{L_{mon}}{L_{spec}}$$

Quality of the Image

Image formation in SEM depends upon detector. Signal (S) is measured by counting electrons falling on detector. The noise (N) reduces the signal and quality is diminished. By increasing number of counts, quality can be improved since it is ratio of signal to noise (S/N).

Contrast is defined as:

$$C = \frac{S_2 - S_1}{S_2}$$

Image formation

SEM forms an intensity map which is two dimensional. Each pixel is indicative of a point on sample which is related to the intensity of sample.

SEM forms a two-dimensional intensity map and each pixel on the map is representative of a point of the sample which is directly related to the intensity of the signal (Fig. 5). It is not possible for SEM to generate a true image rather the image is displayed electronically. SEM determines two characteristic features of a material: Morphology, Topography

4.5 X Ray Diffraction:

XRD analysis is performed to determine the crystallinity of material. XRD shows a researcher that how the atoms are packed in material, bond length and angles.

Instrumentation

Figure below shows the schematics of X-ray Diffractometer

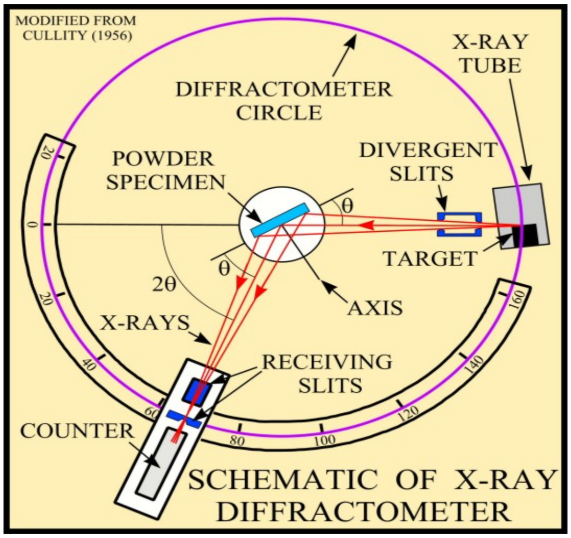

Figure 6: X-Ray Diffractometer Schematics

It has following main components:

1. X-ray Source
2. Monochromator
3. Goniometer
4. Detector

Working principle

Working principle of XRD depends upon inference of monochromatic ray. X-rays are made to fall on the sample placed on monochromator. Every material has different atomic arrangements which depends upon whether a material is crystalline or amorphous. X-rays after striking the specimen reflects and strikes detector. Two phenomena occur in this process, refraction and diffraction. Diffracted rays are absorbed in the material. The diffraction of light varies from material to material and is highly dependent of arrangement of atoms within crystal lattice. Difference between atoms within lattice is measured by Bragg’s law:

$n\lambda = 2d \sin\theta$

n = order of diffracted beam

λ = wavelength of incident x-ray beam

d = distance between adjacent planes of atoms

Material can be easily determined by matching XRD curve with reference pattern

Applications

X-ray diffraction analysis is widely used for following applications

I. To identify unknown crystalline material

II. To Determine unit cell dimensions

III. To check the purity of sample

4.6Fourier Transform Infrared Spectrometry:

In this technique, Infrared is passed through a sample. A part of the IR is absorbed by the sample and rest of it is transmitted. Obtained spectrum shows absorption and transmission, producing a fingerprint of the sample. Like a fingerprint two different structures cannot produce the same IR spectrum. That’s way IR Spectroscopy is very helpful for different types of analysis. FTIR provides the following information

- To identify any unknown material.
- To find the quality of a sample.
- To obtain quantitative analysis of components in any mixture.

The working procedure of FTIR is as:

1. IR beam is emitted from a black-body. It passes through an aperture which controls the amount of energy given to the sample.

2. Then IR beam enters to the interferometer where “encoding” is carried out.

3. The IR beam then enters the sample where it is transferred through or reflected back through the surface of the sample.

4. At last,IR beam then passes through the detector for final image.

5. Finally signal is digitized and sent to the computer where the spectrum is visible.

Because it is a relative measurement scale for the absorption of intensity, therefore a background spectrum must be calculated. As it is a measurement without a sample. It is comparable with the measurement containing sample in beam to find the “percentage absorbance.”

4.7 Crushing Strength:

Tensile testing is characterization technique to determine the mechanical stability of material. In this test material undergoes through stress and the resulting deformation produced from stress is measured. The tensile testing is used to measure the stress-strain curve. Material is taken in standard length and area. The standard length is known as gauge length. Stress is induced in a material at constant rate and strain is recorded. Stress and strain is defined by the following equations:

$$Stress = \frac{Force}{Area}$$

$$Strain = \frac{Change\ in\ length}{Original\ length}$$

Mechanical testing is usually done to get a knowledge about material properties like elasticity, toughness, ductility, and resilience.

4.7.1Universal Testing Machine (UTM)

UTM is used for mechanical testing of material. It consists of the following parts.

I. Frame
II. Engine
III. Gear
IV. Screws
V. Crosshead
VI. Gripping Jaws

VII. Extensometer
VIII. Specimen
IX. Hardware and Software Control

Working principle

The specimen to be tested is placed between jaws of UTM and force in axial direction is applied while recording the resulting strain through computer software. Strain recording is done until material fracture. Relationship between stress and strain is determined through change in length.

Figure 7: Universal Testing Machine (UTM)

4.8 Spectrophotometry:

Dissolution rate was measured by Spectrophotometer. Many methods were available for the determination of urea concentration using spectrophotometry. P-Dimethyl Amino Benzaldehyde method was used to determine the dissolution rate of urea. The method was described as under:

P-Dimethyl Amino Benzaldehyde method:

Urea Standard Solution (A):

Dissolve 1g Urea in demineralised or deionised water and make the volume 1L.

Urea working standard Solution (B):

Take 50ml of solution “A” in 100ml flask and make up the volume with DM/DI water.

P-Dimethyl Amino Benz aldehyde Solution (1% w/v):

Dissolve 1g p-Dimethyl Amino Benz aldehyde in 3ml concentrated HCl. Transfer it to 100ml volumetric flask and make up volume with water.

Hydrochloric acid (1:1):

Carefully dilute 50ml concentrated HCl 100 ml with water.

Calibration Curve:

1. In order to make calibration curve, 2, 4, 6, 8, and 10 ml of urea working solution B was taken in 50 ml volumetric flasks. These solutions were corresponding to 20, 40, 60, 80 and 100 ppm urea respectively.
2. Then add 1ml HCl (1:1) solution and mix it.
3. Add 5 ml p-Dimethyl Amino Benz aldehyde solution and stirred it well. Demineralized water was used to make up the volume of flasks.
4. After 5 min absorbance were noted by using UV –Vis 1900 spectrophotometer at 418 nm. Finally plot the calibration curve between absorbance and known urea concentration in ppm.

Sampling:

In order to find out release rate of S.St urea, S.B urea and S.G urea, following procedure adopted:

1. Took 1L demineralized water in glass beaker.
2. Place it on stirring plate and add magnetic stirrer in it.
3. Take 1g of the sample and add it to 1L demineralized water in the glass beaker

4. Took sample aliquots (10ml) at specified intervals of 6 min, 15 min, 30 min, 60 min (1hr) and 120 min (2hr) from mid depth of sample solution, each in a 100ml volumetric flask and made up the volume with water
5. Before taking the sample for analysis, stir solution gently for 1min at a constant speed to homogenize the solution
6. Finally took an appropriate sample aliquot from sample solution 100ml volumetric flasks for analysis of Urea concentration by UV-Visible Spectrophotometer method as mentioned below.
7. Take 10ml sample (or an aliquot) from 100ml flask in a 50ml volumetric flask and proceed through 2-6 in calibration curve method.
23. Dissolution rate was measured by using absorbance data against calibration curve relationship:

Urea (ppm) = [(Absorbance - y-intercept)/Slope] [39].

Chapter 5: Results and Discussions

This chapter focuses on the results obtained by using various analytical techniques are discussed and reviewed significantly.

5.1 Surface Morphology:

For the topography of both coated and uncoated samples, Scanning Electron Microscopy was used previously [38]. In this study, SEM is used to analyze the topography of urea granules. Morphological studies of coated and uncoated urea were carried out at x100 and x2500 magnification to estimate structure of the coating films on coated granules by using Scanning electron Microscope. SEM examinations gave improved picture of surface structure and pores exhibition.

A SEM (S-4700 Hitachi, Japan) was utilized for the morphological examination of coated urea samples. Uncoated urea granules were also examined prior to coated samples for reference. Then coated urea was analysed with a secondary electron detector using the accelerating voltage of 20 kV.

The SEM images of Uncoated and coated urea granules (from S-4, S-6 and S-8) were shown in Figure-8.

Because granular urea production involves agglomeration due to fluctuations in controlling parameters (temperature and air flow rate) of the granulator, this suggests the lump formation (Fig. 2(a)).The pointy crystals of the sample S-4 are sintered with fine crystals on top of the urea (Fig. 2(b)). Few pores are also present due to non-homogeneous coating and it is due to manual dip coating technique. These onions like layers are due to the presence of Plaster of Paris. For sample S-6, the particles under observation, are edgy and rough along with some large slabs randomly present and can be seen (Fig. 2(c)). Fig. 2(c) also shows that the coated layer is thick, and some visible gaps or cavities are also present in coating layer. Dense coating layer formation is due to the presence of molasses. The particles look rough with clear needle like crystals which can be observed throughout the surface of the urea sample (Fig. 2(d)). As compare to S-6, the surface of S-8 is smoother, but some cavities are also observed, which shows the non-homogeneity of the coating layer due to the lesser quantity of PVA(only3%) which forms a thin layer that acts as a membrane (Fig.2 (d)).

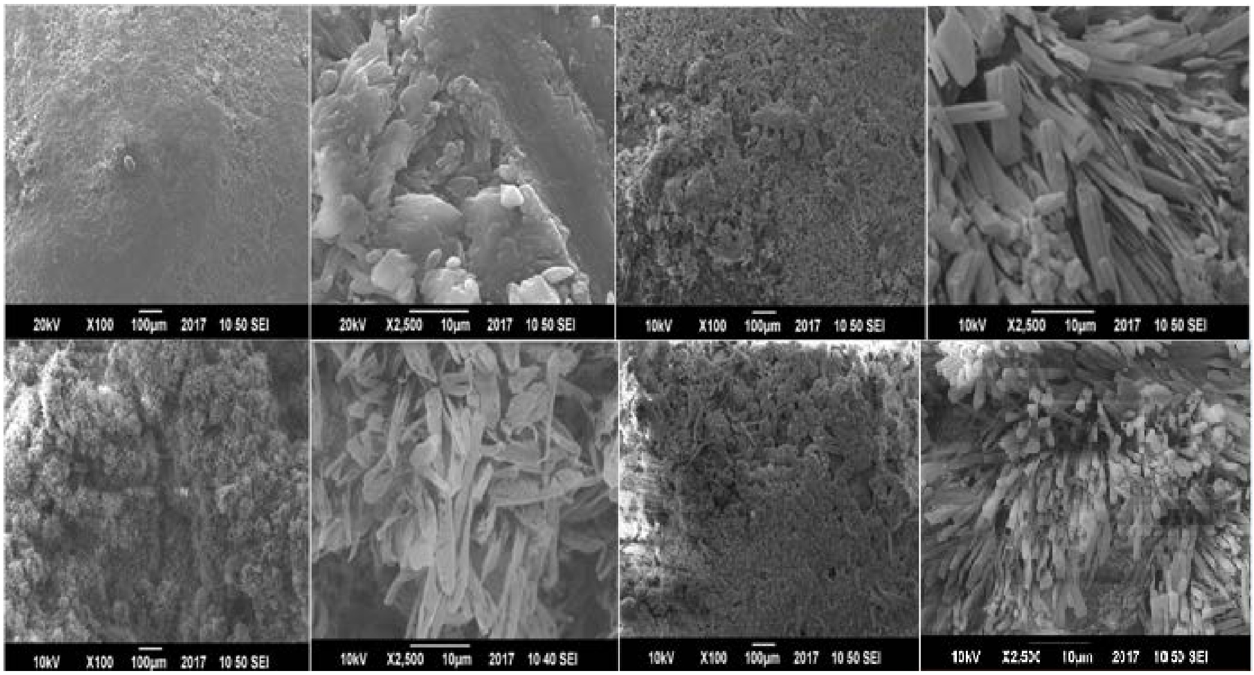

Figure 8 : SEM micrograph of Uncoated and coated urea

The bigger pointy crystals observed are due to the presence of Sulphur and can be estimated as the surface of urea. It is also observed that the imperfect coating provides a channel for the escape of urea through these cavities by contact with irrigation water. The SEM image of S-8(Fig. 2(d)) shows that there is compact surface b/w the coating layer and the urea surface with no cavities b/w them. Outer surface of S-8(Fig. 2(d)) observed is comparatively smooth with a small lump observed at surface. Surface of S-6(Fig. 2(c)) is coarse due to the large quantity of PVA (5%) with larger lumps as compare to S-8.

5.2Dissolution Rate of Nutrient Nitrogen:

To examine nutrient dissolution rate from coated urea, a conductivity analysis carried out [49]. To find the release rate conductivity was measured over a specific time interval. The conductivity value fluctuated as the ammonium and nitrate ions were discharged in de-ionized water through the coated films. To evaluate the conductivity, 50 ml of de-ionized water was taken in a beaker and 5 grams of coated urea was added in it. After that Conductivity was noted at specified time.

The release rate of Nitrogen in terms of ammonium and nitrate ions was calculated and results were depicted in Table 3 and Figure 9. The total test was performed for time span of 50 minutes. As it can be seen in the figure 9 that the release rate of sample-3 was lowest among all samples. (Figure5-2).After 30 minutes the conductivity values of S-3 became constant till the experiment was over. The conductivity of sample-6 was on greater side among all samples.

Table 3: Release Rate of Nutrient Nitrogen

Time Min.	Uncoated MS/cm	S-1 MS/cm	S-2 MS/cm	S-3 MS/cm	S-4 MS/cm	S-5 MS/cm	S-6 MS/cm	S-7 MS/cm	S-8 MS/cm
0	2.03	2.53	1.86	2.09	1.75	1.96	1.88	1.64	1.62
10	10.6	9.9	4.72	13.6	3.46	3.67	3.1	3.83	4.04
20	11.53	13.02	5.67	23.5	3.85	3.97	3.16	3.93	7.15
30	11.58	15.05	7.33	31	3.99	4.07	3.2	4.05	8.15
40	11.58	15.06	7.34	31.02	3.99	4.07	3.2	4.05	8.15
50	11.58	15.06	7.34	31.02	3.99	4.07	3.2	4.05	8.15

Figure 9 : Release Rate of Nutrient Nitrogen

Conductivity analysis was done for finding release rate of uncoated and coated urea granules at 0, 10,20,30,40 and 50 minutes for the samples S-0 to S-8 respectively. From results it can be concluded that uncoated urea was released completely around 5-6 minutes as its conductivity valuesbecameconstantafter10minutes. From S-1 it can be concluded that most of the urea released around 12-15 minutes as the value became constant after 20 minutes which shows that urea has released completely till 20 minutes.

From the conductivity analysis of S-2 it is determined that most of the urea released around 20-22 minutes as the conductivity value became constant after 30 minutes which shows that urea has released completely till 30 minutes.

For S-3 it can be determined that most of the urea released around 22-25 minutes and the value became stable after 30 minutes which shows the complete release of urea. Results of samples S-4 to S-7 were not satisfactory and their release rate was fast.

From the conductivity analysis of S-8 it may be determined that most of the urea released till around 14-16 minutes as the value has become constant after 20 minutes which shows that urea has released completely till 20 minutes.

From conductivity graph of all 9 samples it is clear that samples containing optimum quantity of PVA with Plaster of Paris as a binder had comparatively better results of dissolution rate of coated urea granules as compare to coated urea contained molasses as binder. It is due to the reason that Plaster of Paris forms thick, hard and crunchy coating layer when use as a binder. Whereas molasses forms a thin, soft and flexible coating layer which has less effect on release rate of urea.

5.3Spectroscopy:

Spectroscopy was also used to determine dissolution rate of coated and uncoated urea samples as the results obtained through conductivity method were not interpreted properly. Spectrophotometer UV-1900 was used to measure the release rate. Many researchers used this method. Especially for the unknown concentrations of urea, spectroscopic analysis was more convenient and effective.

Table 4: Calibration curve data by using industrial method

Sr. No.	Urea (PPM)	Absorbance (Au)
1	20	0.013
2	40	0.033
3	60	0.047
4	80	0.059
5	100	0.068

Figure 10 illustrated the calibration curve for the known concentrations of urea against its absorbance by using UV-spectrophotometer.

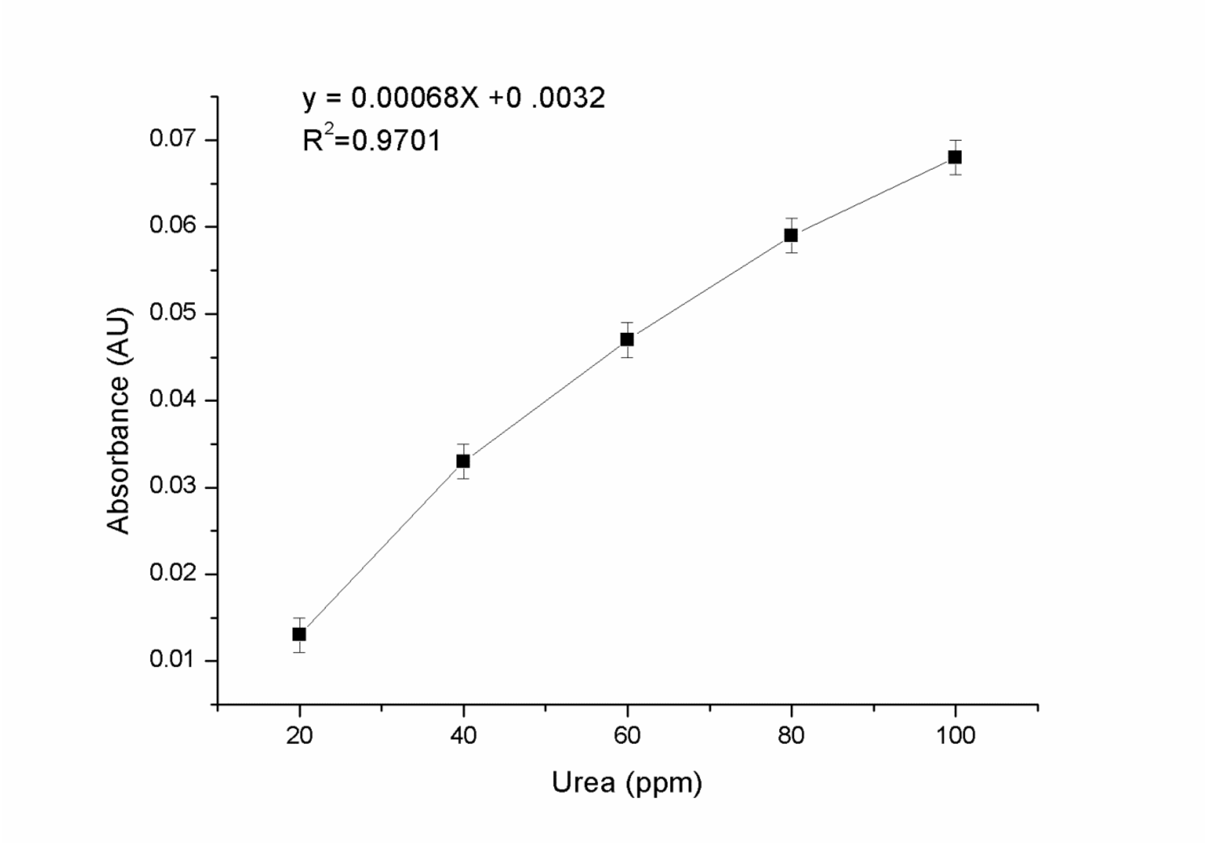

Figure 10: Calibration Curve for slope measurement

The above calibration curve is used to find out the slope by using equation Urea (ppm) = [(Absorbance - y-intercept)/Slope] [39].

Table 5 : Concentration (ppm) of uncoated urea and coated urea at different intervals of time

Sample Name	Time 3 min	Urea Con(ppm)	6 min	9 min	12 min	15 min	30 min	1 hr	2 hr
Uncoated Granular	12.3	Urea Con(ppm)	19.8	33.1	69.9	80	80	80	80
S-1	7.75	Urea Con(ppm)	9.41	11.9	67.75	80	80	80	80
S-2	6.77	Urea Con(ppm)	9.82	20.9	38.2	56.2	75.6	80	80
S-3	3.25	Urea Con(ppm)	7.91	11.2	46.43	62.21	75.55	80	80
S-4	3.79	Urea Con(ppm)	8.88	11.4	33.2	44.65	65.87	80	80

S-5	7.28	Urea Con(ppm)	9.56	24.41	51.25	60.11	77.1	80	80
S-6	3.5	Urea Con(ppm)	4.5	9.9	18.75	48.7	63.33	70.0	80
S-7	6.9	Urea Con(ppm)	17.8	28.6	45.6	67.9	80	80	80
S-8	4.9	Urea Con(ppm)	7.99	15.6	29.5	49.6	67.3	79.4	80

Figure 11 showed the relationship between uncoated urea concentrations (ppm) verses time (min). The dissolution rate is directly related with the absorbance of the urea solution. Higher the absorbance of the urea solution greater will be the concentration of urea in solution and vice versa [38, 39]. This is just because of that uncoated urea has exposed surface that provides higher penetration of water molecules. At different time intervals urea release measured in terms of absorbance which showed increasing dissolution rate.

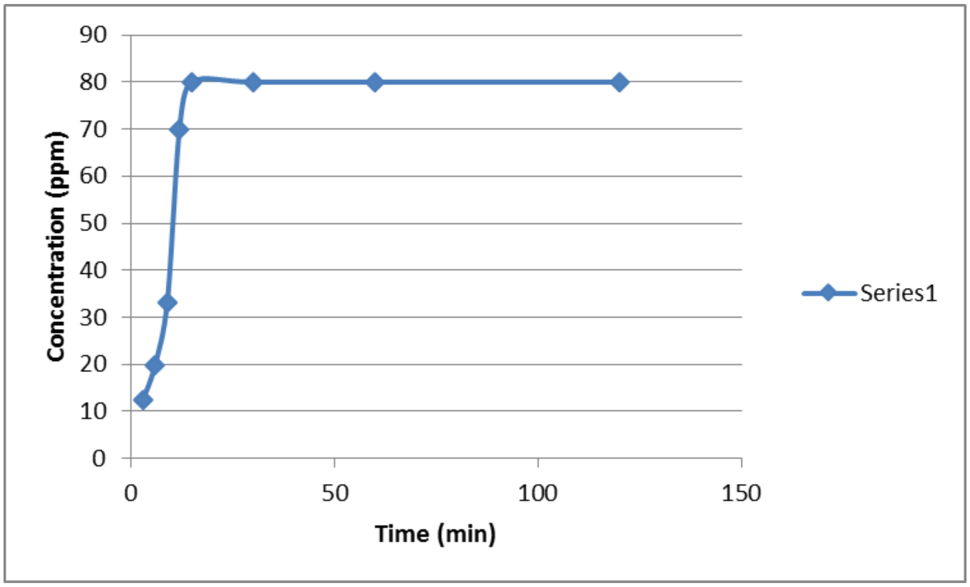

Figure 11 : Uncoated Urea release: Time (min) Vs Urea Concentration (ppm)

Figure 12 showed the release behavior of S-3 urea in terms of absorbance with respect to time. Initially S-3 urea dissolved slowly as compared to uncoated urea. This was due to the coating layer containing 04% PVA and 02% Plaster Of Paris (POP) which provided a barrier in urea release through matrix into the bulk solution phase. During first interval

(6 min) the coating layer suppressed the nutrient release. Similar pattern observed for the adjacent intervals of time. Because of the hydrophilic nature of starch the coating layer starts to disintegrate and provided the channels for water penetration inside the coating layer. Water penetrated inside the coating matrix and released the nutrient at much higher pace as compared to initial release rate. Slow release pattern observed but not up to satisfied level just because of the weak bonding of coating layer.

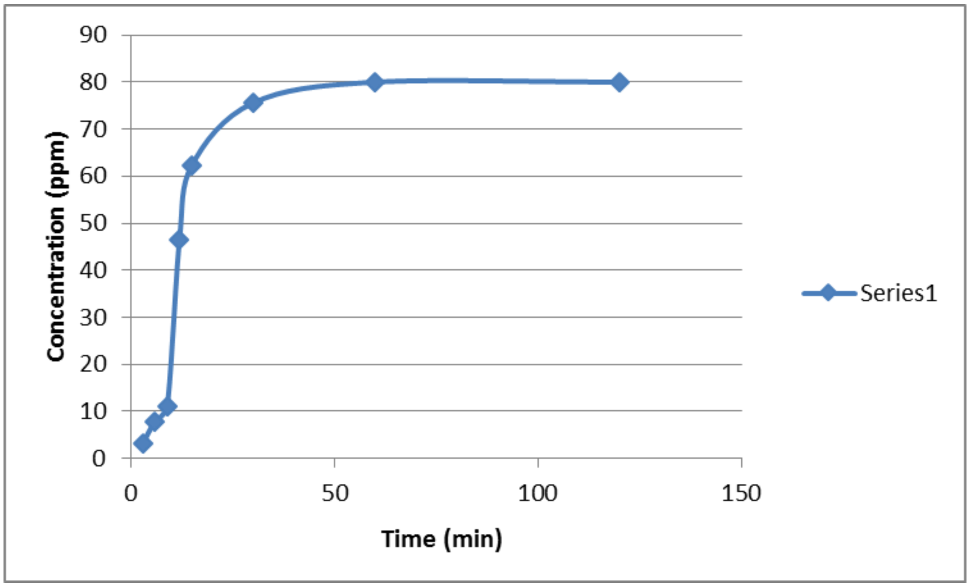

Figure 12: Urea release: Time (Min) Vs Urea Concentration (ppm)

Figure 13 illustrated the release pattern of S-4 urea in which urea granule was coated by 03% PVA in the presence of 02% Plaster Of Paris (POP) binder. A notable decrease in dissolution rate was observed in this case. Since POP was soluble in water and had good binding characteristics it concealed the urea release [43]. A good periodic release behavior was observed which made POP as a good binder.

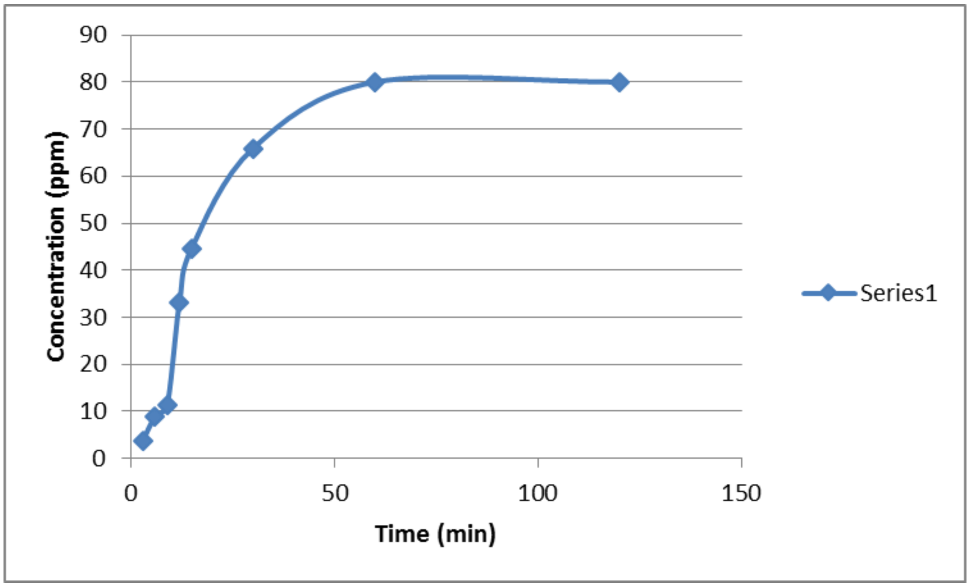

Figure 13 : Urea release: Time (Min) VS Urea Concentration (ppm)

Figure 14 showed the urea release trend of S-6 urea in water. Urea granules were coated with coating solution in the presence of molasses as a binder and then applied to water to observe its dissolution rate. At first interval S-6 urea showed least dissolution rate as compared to uncoated, S-3 urea and S-4 urea. This was because of the homogeneous coating layer & plasticity behavior of molasses which resisted the penetration of water molecules to the inner core through matrix. A membrane like structure observed that narrowed the path flow of solvent molecules to travel to the inner core. This was resulted into slow release of urea granules due to channeling. Molasses as a binder increased these channels length and enhanced the effectiveness of coating material. Molasses swallowing ability helped to make this membrane like structure.

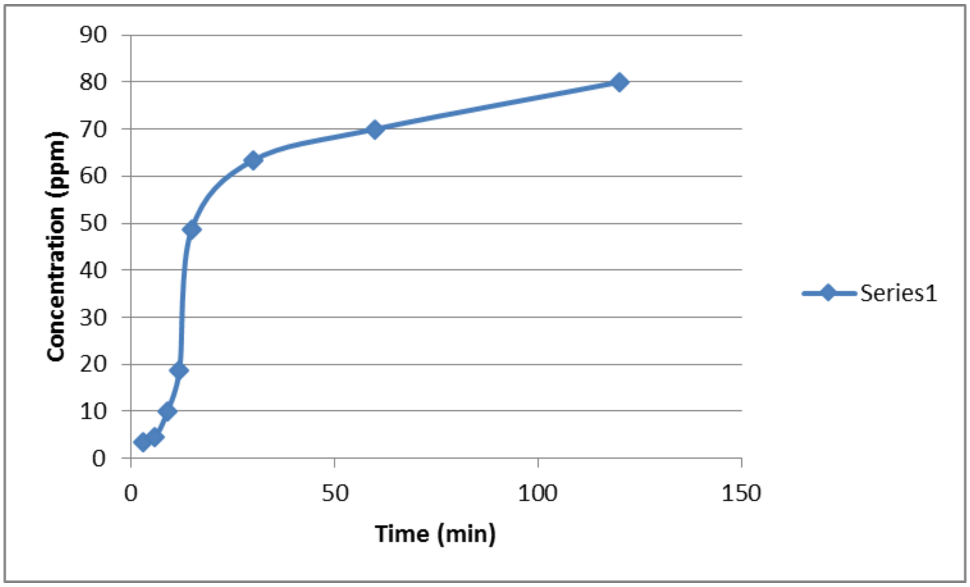

Figure 14 :Urea release: Time (Min) VS Urea Concentration (ppm)

Dissolution rate comparison of uncoated and coated urea plots were shown in following Figure 15**:**

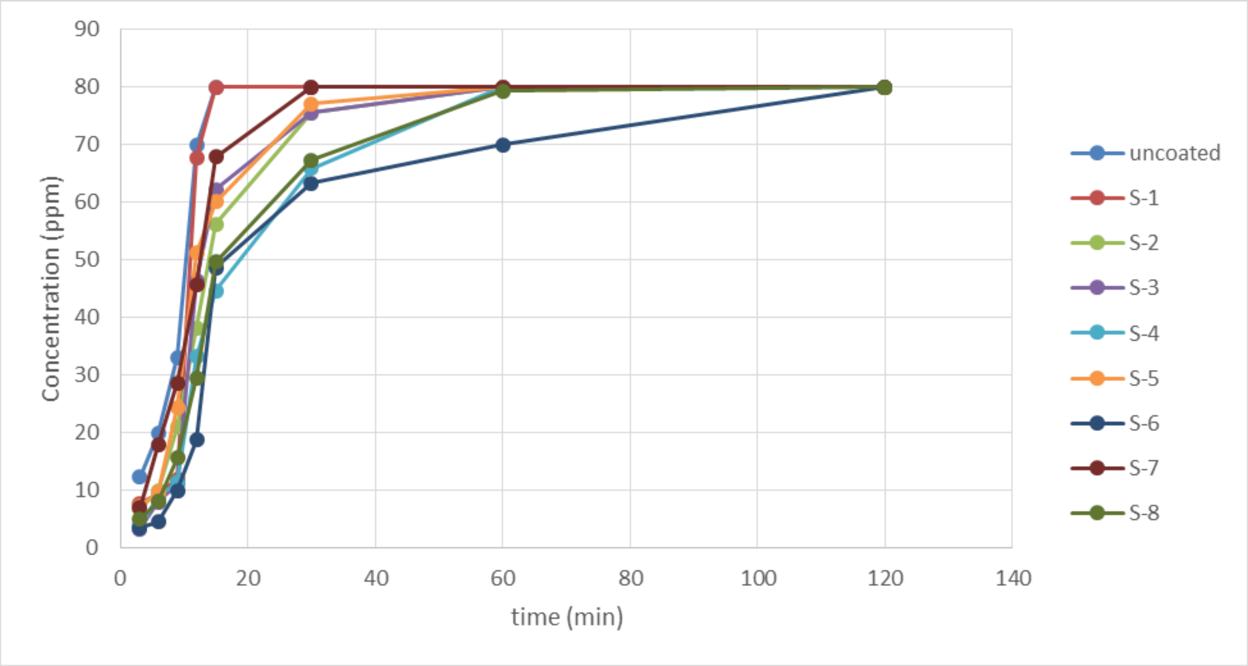

Figure 15 : Comparison between Coated and Uncoated Urea Samples: Time (min) VS Urea Concentration (ppm)

Figure 15represented the comparative release pattern of uncoated urea and coated urea. It was revealed that S-6 urea gave slowest release rate among all the coated samples. According to spectroscopy results the best coating materials obtained by using Dip Coating Technique were PVA and Molasses.

5.4 Crushing Strength:

Crushing strength of coated urea samples was measured using a Universal testing machine (AGX Plus). The crushing test is significant to make sure that the finished granules can bear up the physical handling all the way through packaging, storage and delivery. During testing, the each fertilizer granule was exposed to a calculated force by means of metal plunger. The point where the granule broke was known as its maximum strength.

The crushing strength is important factor in a sense that during bagging and transportation process, a lot of dust is formed and particles are crushed that cause handling problems as well as loss in coating material and nutrients. Loss of valuable coating material results into decrease in profitability of final product as well as the thickness of coated urea. The objective is to increase crushing strength and to improve the mechanical properties of urea.

Table 6: Crushing Strength of uncoated and coated urea

Sample Name	**Crushing Strength (Newton)**
S-0	**104.7**
S-1	**126.4**
S-2	**128.5**
S-3	**155.9**
S-4	**158.5**
S-5	**127.1**
S-6	**132.9**
S-7	**136.8**
S-8	**152.2**

Figure 16 : Crushing Strength of coated and uncoated urea

Significant increase in crushing strength of coated urea samples was observed as compared to uncoated urea. Samples S-3, S-4 and S-8 showed the best results.

Coated samples containing Plaster of Paris (samples S-1 to S-4) showed high crushing strength as compared to those that contain molasses (samples S-5 to S-8). It is due to the reason that Plaster of Paris imparts hardness to materials when dried as compared to molasses.

From crushing strength graph it can be concluded that by decreasing PVA contents, the crushing strength of both molasses and Plaster of Paris increases. It is due the film forming property as well as plasticizing ability. That’s why it does not impart hardness to materials due to its long polymeric chains.

From samples S-1 to S-8, only two samples (S-4 and S-8) showed highest crushing strength as these samples contain minimum quantity of PVA(only 3% by weight) with 2% Plaster of Paris by weight in S-4 and 2% molasses by weight in S-8 as shown by the following graph trends.

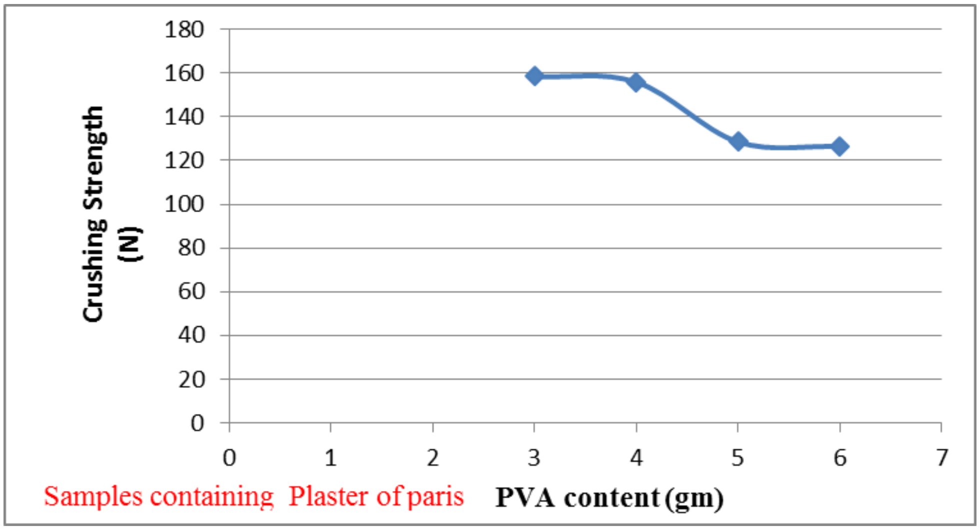

Figure 17 : Crushing Strength with (POP)

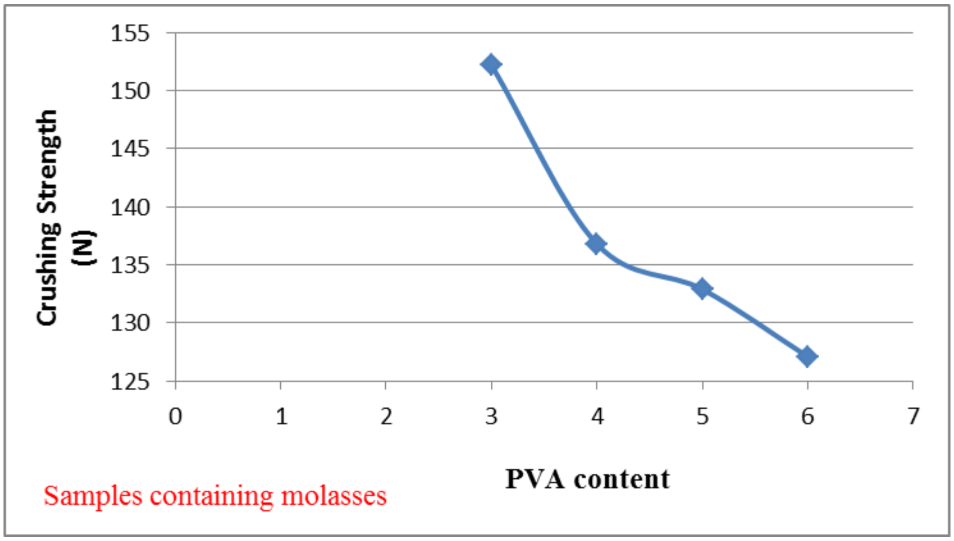

Figure 18 : Crushing Strength with molasses

5.5 FTIR spectroscopy of Coated Urea:

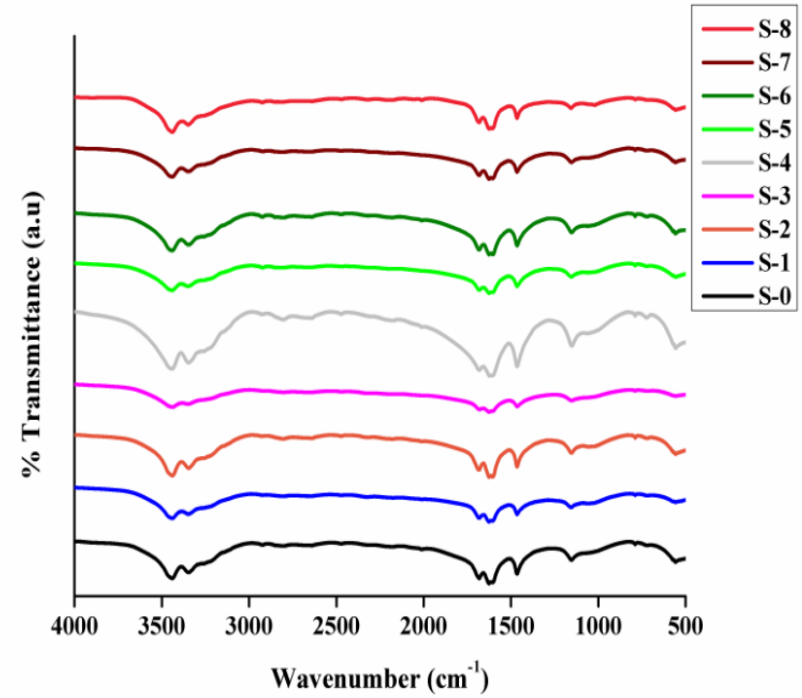

Figure 19: FTIR Spectroscopy of Uncoated and Coated Urea

Urea is an essential fertilizer for plant growth. The main problem that farmers are facing with urea is release rate of nitrogen contents from urea, so for the purpose of slow release of urea, coating layer is applied on urea that mainly consists of starch and different composition of polyvinyl alcohol.

Fourier Transform Infrared spectroscopy of Samples S-0 to S-8 was obtained for the dried powder using a FTIR Perkin Elmer Spectrum 100 spectrometer.

FTIR graph of S-1 in which the peak at 3439.42 shows the stretching of -OH alcoholic bond and at 1626.31 cm^{-1}, intermolecular hydrogel peak is formed which indicates the bonding b/w between PVA and large molecules of starch. The peaks at 1154.85 cm^{-1} comes in the range of C-H-O bond stretching.

In sample S-2, two strong peaks in the region of 3300 to 3450 cm^{-1} are due to OH stretching bond of polyvinyl alcohol while the bonds in 1600 cm^{-1} range indicates intermolecular hydrogel and C-C bond stretching is due to the presence of starch molecules. The strong peak at 1625.29 indicates the strong bonding between starch and polyvinyl alcohol.

The result of S-3 is similar to that of S- 1 with high transmittance which indicates that less bonds are absorbing light.

S-4 shows result at low transmittance. As indicated by the figure, more bonds are absorbing light and more peaks are formed. The additional peak at 2802.96 indicates the C-H bond stretching.

In S-5 same bonds as mentioned in above three diagrams with low transmittance that may be due to the property or state of material. The broad peak at 3439 cm^{-1} shows the strong hydrogen bonding in that region which indicates that water may be present here.

In S-6 the region behind 500 cm^{-1} is the finger print region and the region of 1465 cm^{-1} indicates the C-H-O bond vibration while peak at 3440 cm^{-1} shows the -OH bonding.

S- 7 and S-8 show almost same peaks with -OH bond stretching in 3439 cm^{-1}, intermolecular forces b/w between starch and polyvinyl alcohol at 1625 cm^{-1} C-H-O bonds vibrations at 1465 cm^{-1}

5.6XRD

XRD characterization of PVA/Starch blend coated urea was carried out. Scan angle was varied b/w 20º to 70º. Step size and step time was taken as 0.4 degree and 1 second respectively. For characterization, radiation used was of Cu K α-1 [6].

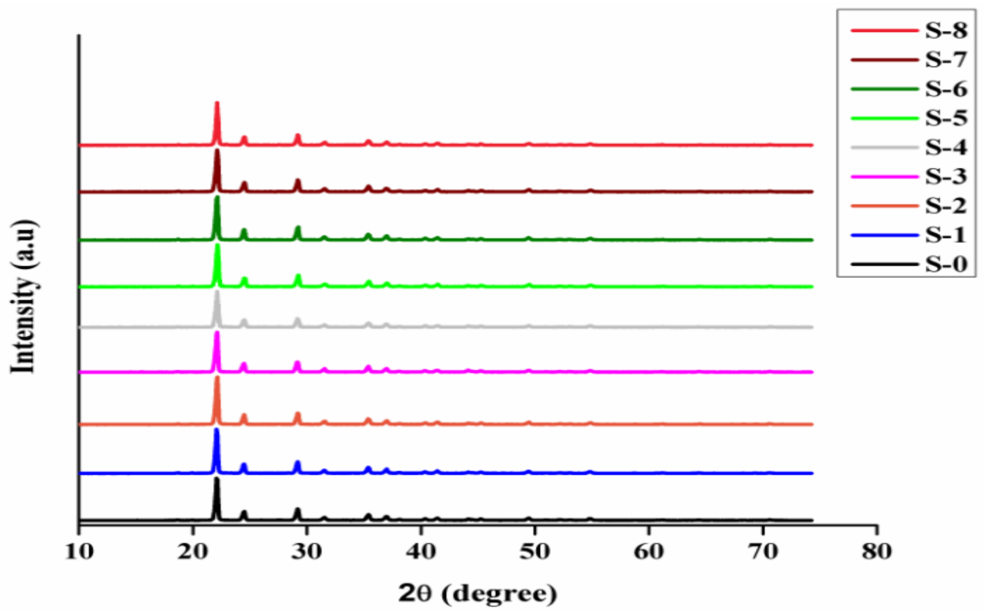

Figure 20 : XRD of Uncoated and Coated Urea

Fig. 20 shows XRD patterns of PVA, Starch, Sulphur and different binders coated film on urea granules cross-linked with Sulphur content 05 wt. %, respectively. There are peaks of Starch overlapping an amorphous hump. As Poly Vinyl Alcohol is a semi crystalline polymer and has much more physical interactions b/w the polymer chains, due to hydrogen bonding b/w the hydroxyl groups. Poly Vinyl Alcohol has a diffraction peak at 2Theta = 20 degree, and is characteristic for an orthorhombic structure .From above figure it can be concluded that the Crystallinity does not change after mixing with other coating materials. As there is no change in Crystallinity of Poly Vinyl Alcohol which indicates that structure was not changed after cross-linked with other coating materials and starch. While formation of film, bonding was formed b/w starch and PVA that may result of decrease in the number of hydrogen bonds, hence the Crystallinity of PVA indicates strong bonding present b/w starch and PVA polymer chains by cross linking.

5.7Moisture Content

The moisture contents of the uncoatedand coated urea granules were evaluated by drying 1 g of the each sample in an oven at 110 ± 2°C for 4 hours and moisture loss was observed as given in the following table as well as in graph.

Table 7: Moisture Lost Measurement

Analysis of Moisture Content						
Temperature 110°C for 4 hours						
Sample	**Wt % PVA**	**Wt of Empty dish (gm)**	**Weight of sample before heat**		**Weight of Sample**	
			Weight of sample (gm)	Weight of sample and dish **(gm)**	**Weight with dish after 4hrs (gm)**	**Moisture Lost**
S0	0	44.336	1.006	45.342	45.32	0.022
S1	6	46.565	1.006	47.571	47.545	0.026
S2	5	49.727	1.005	50.732	50.712	0.02
S3	4	49.914	1.004	50.918	50.9	0.018
S4	3	48.674	1.004	49.678	49.66	0.018
S5	6	51.82	1.007	52.827	52.725	0.102
S6	5	44.2833	1.002	45.2853	45.269	0.0163
S7	4	31.865	1	32.865	32.845	0.02
S8	3	42.103	1	43.103	43.08	0.023

Figure 21: Moisture Lost

Chapter 6 - COST ESTIMATION

6.1 COST ESTIMATION OF COATED UREA:

Total Cost of coated urea = Cost of uncoated urea + Cost of coating solution + Operational Cost (Electricity)

Weight of uncoated urea = 50 kg

Required Materials for coating Solution:-

Starch = 10 g/500 g

Molasses = 2 g/500 g

Plaster of Paris = 2 g/500 g

Sulphur = 5 g/500 g

Polyvinyl Alcohol (PVA) = (6, 5, 4, 3) g/500 g (PVA will be used in different concentrations)

Starch:

Starch required for 500 g coating = 10 g

Starch required for 1g coating = (10/500) g

Starch required for 50,000 g coating = (10/500) * 50,000 = 1000 g OR 1 Kg

Price of 1 kg starch = 1000 PRs/-

Molasses:

Molasses required for 500 g coating = 2 g

Molasses required for 1g coating = (2/500) = 0.004 g

Molasses required for 50,000 g coating = 50,000 * 0.004 = 200 g = 0.2 kg

Price of 1 kg molasses = 3500 PRs/-

Price of 0.2 Kg molasses = 3500 * 0.2 = 700 PRs/-

Sulphur:

Sulphur required for 500 g coating = 5 g

Sulphur required for 50,000 g coating = (5/500) * 50,000 = 500 g = 0.5 kg

Price of 1 kg Sulphur = 1000 PRs/-

Price of 0.5 kg Sulphur = 1000 * 0.5 = 500 PRs/-

Plaster of Paris:

P.O.P required for 500 g coating = 2 g

P.O.P required for 50,000 g coating = (2/500) * 50,000 = 200 g = 0.2 kg

Price of 1 Kg P.O.P = 140 PRs/-

Price of 0.2 Kg P.O.P = 140 * 0.2 = 28 PRs/-

Total cost for the above mentioned materials = 28 + 500 + 700 + 1000 = 2228 Rs/-

Polyvinyl Alcohol:

6g

PVA required for 500 g urea = 6 g

PVA required for 50,000 g urea = (6/500) * 50,000 kg = 600 g = 0.6 Kg

Price of 1 kg PVA = 13000 PRs/-

Price of 0.6 kg PVA = 13000 * 0.6 = 7800 PRs/-

Total Cost for 50 kg coating = 7800 + 2228 = 10028 PRs/-

5g

PVA required for 500 g urea = 5 g

PVA required for 50,000 g urea = (5/500) * 50,000 kg = 500 g = 0.5 Kg

Price of 1 kg PVA =13000 PRs/-

Price of 0.5 kg PVA = 13000 * 0.5 = 6500 PRs/-

Total Cost for 50 kg coating = 6500 + 2228 = 8728 PRs/-

4g

PVA required for 500 g urea = 4 g

PVA required for 50,000 g urea = (4/500) * 50,000 = 400 g = 0.4 kg

Price of 1 kg PVA = 13000 PRs/-

Price of 0.4 kg PVA = 13000 * 0.4 = 5200 Rs/-

Total Cost for 50 kg coating = 5200 + 2228 = 7428 PRs/-

3g

PVA required for 100 g urea = 3 g

PVA required for 50,000 g urea = (3/500) * 50,000 = 300 g = 0.3 kg

Price of 1 kg PVA = 13000 PRs/-

Price of 0.3 kg PVA = 13000 * 0.3 = 3900 PRs/-

Total Cost for coating of 50 kg of urea = 3900 + 2228 = 6128 PRs/-

Electricity Cost (for making of coating solution through hot plate):

Hot plate load= 650 W

Coating solution making time= 2hrs

Energy consumed by hot plate= 1.3*2= 2.6kWh (unit consumed) (for making coating solution for 500g of urea)

Energy consumed by hot plate for making coating solution for1kg of urea=2.6*2=5.2 kWh

Cost of 1 kWh= 8 PRs/-

Electricity Cost for 1kg coated urea = 5.2*8= 41.6 RS/-

Electricity Cost for 50kg coated urea =41.6*50=2080

Grand total cost of coating solution for coating 50kg of urea= 6128+2080= 8208 PRs/-

Cost of 50kg of uncoated urea=1300 PRs/-

Total cost for making 50kg of coated urea= Cost of uncoated urea+ Cost of coating solution= 1300+8208= 9508Rs/-

Chapter7: Conclusions and Recommendations

2. 7.1 Conclusions:

Objective of my MS Thesis was to study the effect of PVA/Starch blends on slow release urea fertilizer. I selected best coating materials like Plaster of Paris, Sulphur, Molasses, Poly Vinyl Alcohol (PVA) and Starch. These materials were used to prepare coating solution and were analysed in different combinations in which sulphur acted as a base material due to its ability to enhance the fertility of the soil. 8 solution samples were prepared with different percentages of PVA and 2% binder was also used and release rate was tested by Conductivity method.

SEM and release rate measurement showed that Samples containing Molasses as a binder had better slow release characteristics than others. Sample no.6 was observed as the best in terms of release rate.

SEM and release rate measurement results indicated that by varying the PVA quantity and by change the type of binder, dissolution rate was changed. This was more than the previously reported i-e 26% in literature. Better compactness was observed by keeping the optimum quantity of PVA. An increase in surface strength was also observed by SEM images.

A significant increase in crushing strength was observed in case of S-4. It showed that the coated urea can withstand enough force until breakage occur in this way materials wastage will be less during handling and transportation steps. It also reduces the cost of coating materials and increases the efficiency in terms of release rate.

3. 7.2Recommendations:

This project motivates to think about other aspects of producing slow release urea fertilizer in the following ways:

- The coated urea would be prepared by using spray coating technique to enhance its efficiency.
- The coated urea would also be prepared by using a fluidized bed coater to increase its efficiency
- Dry coating method would be more beneficial in order to develop slow release fertilizer.

- Better temperature control would be achieved by using a fluidized bed coater that could reduce dissolution rate of urea.

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