Synthesis and characterization of Zinc coated urea fertilizer to overcome micro-nutrient deficiency and improve urea nitrogen use efficiency

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Synthesis and characterization of Zinc coated urea fertilizer for induction of zinc micronutrient to soil and improvement in nitrogen use efficiency

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DEDICATION

“This thesis is dedicated to family, teachers and friends for endless motivation, support and encouragement throughout the research”

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Abstract

Urea consisting 46% Nitrogen (N) by weight is the most common and principal nitrogen rich fertilizer used in today’s world. Almost half of world population use it to increase the productivity of crop. However with low nitrogen use efficiency of urea and severe micronutrient deficiencies like Zinc (Zn), the productivity has not been up to the mark and nutritional quality of foods from these crops is very low. The early decomposition and fast release rate not only leads to decreased nitrogen use efficiency but also leads to contamination of ground water and hazardous emissions to atmosphere. Similarly the micronutrient deficiencies like Zn are transferred from soils to plants and to humans and animals who feed on the foods from these plants. This pose a major threat for agriculture globally and future food security.

For this purpose, seven coated urea fertilizers Zinc oxide-coated (ZnO), Zinc oxide sonicated-coated (ZnO-Son), Zinc oxide with Gelatin-coated (ZnOG), Gelatin-coated (G), Zinc oxide with molasses-coated (ZnOM), Zinc sulphate with molasses-coated (ZnSM) and Zinc sulphate-coated (ZnS) urea were prepared using different coating solutions in a fluidized bed coater. All samples were characterized through SEM to check the surface morphology of coated fertilizer and examined through XRD and FTIR techniques to observe compositions and interactions between urea and coating materials. Crushing Strength tests were carried out to verify if coated samples could withstand the physical impacts of inventory and transportation operations.

Pot tests with Rye grass as test crop were also carried out to evaluate effect of coating on yield, N and Zn uptake. Soil samples were also taken to determine Zinc content in soil for each applied fertilizer sample.

Characterization tests verified the presence of component materials in the coated samples and physical nature of interaction between urea and coated materials. ZnOG was the best sample in terms of yields , N and Zn uptake and Nitrogen use efficiency. All the samples of Zinc oxide resulted in improved response in terms of plant yields, N and Zn uptake.

Keywords: Nitrogen use efficiency, Zinc (Zn), Micronutrient deficiency, Coated urea, Nitrogen and Zinc uptake, Gelatin.

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Abbreviations

N	Nitrogen
Zn	Zinc
UC	Uncoated urea
C	Control
ZnO	Zinc oxide coated urea
ZnO-Son	Zinc oxide sonicated coated urea
ZnOG	Zinc oxide with gelatin coated urea
G	Gelatin coated urea
ZnOM	Zinc oxide with molasses coated urea
ZnSM	Zinc sulphate with molasses coated urea
ZnS	Zinc sulphate coated urea
SEM	Scanning Electron Microscope
EDX	Energy-dispersive X-ray spectroscopy
FTIR	Fourier Transform Infra-Red
ANR	Apparent Nitrogen Recovery
AZnR	Apparent Zinc Recovery
DMY	Dry Matter Yield
FMY	Fresh Matter Yield

Chapter 1

Introduction

In recent decades, population has been increasing at alarmingly high rates bringing attention to need of effective fertilizers to meet high demands of food [1]. For growth of plants and good crop yields, both macro nutrient and micro nutrient fertilizers are essential in different proportions. It is estimated that globally almost 30-50% of crop yields are because of application of fertilizers. Urea has been the most relied upon nitrogen source fertilizer in agricultural world due to its high availability, low cost and high nitrogen concentration. With rapid population growth estimated as to cross 9 billion by 2050, the demand for urea consumption is estimated to increase to 130 million to 150 million tons per year [2].

However pure conventional urea has very low effectiveness with 50-70% of applied nutrient lost to environment [2]. This means that we do not apply urea according to crop needs rather loose most of the nutrients to environment with crop up-taking very less amount of the total applied urea. Urea losses can be reduced by increasing frequency of application with small quantities but the costs associated with application and spreading are very high [3]. The losses occur through ammonia volatilization, leaching, denitrification and runoff. These losses result in contamination of ground water by $NO3^-$ leaching and emission of hazardous gases NH_3 and N_2O to environment. These loses not only pose serious environmental threat but also long term economical losses. These losses occur due to premature decomposition of urea due to action of urease enzymes along with water which leads to ammonia volatilization before nutrients can be adsorbed by plants. Multiple parameters like soil pH, rain or moisture content, soil microbiology are important in governing the losses. Rain reduces the potential for volatilization losses and denitrification is enhanced at pH greater than 7. Increasing nitrogen use efficiency will lead to more N uptake resulting in increased yield for same fertilizer application rate or maintained yield for less fertilizer application rate.

Low efficiency of urea is not the only obstacle in achieving the production and nutrition quality goals for sustainable agriculture system. The continuous intensive cropping has resulted in severe depletion of soil's own micronutrients and has been a barrier in achieving production goals. The plant parts i.e. root, shoot, leaves uptake required nutrients through different mechanisms from soil. Either these micronutrient are exhausted or are present in non-available forms for plants. These deficiencies has not only affected the crop yields but has led to micronutrient malnutrition in population of developing countries leading to various health problems. Micronutrient malnutrition could lead to multiple social and health problems i.e. poor immune system and mental retardation. Zinc is one of the most common and critical deficiency in soils and plants and a major constraint in global food production [4]. Almost 49% of the cultivable soils are deficient in zinc [5]. In analysis of 250,000 soils and 25000 plant samples in India, 48% of soil and 44% of plant samples were deficient in Zinc with other micronutrient deficiencies i.e. Fe, Cu and Mn standing at 11%, 7% and 5% respectively [6]. This deficiency results in low nutrition crops and causes malnutrition in humans depending on them as a food and nutrition source. According to a report of WHO (2002), Zinc deficiency is the fifth most significant risk factor for illness and death in developing countries. The widespread zinc deficiency in children is a major cause of death in the world [7]. According to WHO, approximately 80,000 people annually die due to zinc deficiency among which are 450,000 children are below age of five. According to another estimate, globally 3 billion people suffer from Zinc deficiency [4].

The conventional urea can be made much more efficient by coating it with materials which can act as barrier and slow its solubility and with micronutrients like zinc which can have significant impact on the productivity and nutrition quality of the crops. Increased Nitrogen efficiency will lead to less environmental threat and low economic losses while micronutrients incorporation will improve the over health and nutrition of humans along with plant yields.

1.1 Background

The rapid growth of population has led to high food demands. Along with high food demands, urbanization and industrialization has led to deforestation and expansion leading to food deficiencies. These deficiencies and gaps are further hit by climate change effects i.e. flooding and pest attacks. To meet these food demands with ongoing population growth, climate effects and urbanization, intensive cropping system with high fertilization has been opted. The intensive cropping system has exhausted the soil's micronutrients and has led to low productivity and low nutrition crops [8]. Urea with low nitrogen use efficiency has been over applied to crops with most of the nutrients lost to environment posing serious threat to environment along with economic losses. Resources of significant importance like natural gas used in manufacturing of urea are indirectly and irreversibly lost along with loss of urea. Farmers generally don't apply micronutrients like Zinc separately due to lack of awareness, extra labor costs required for spreading and application, low quality and high costs of Zinc sources. Owing to zinc deficiency, the agriculture productivity and human health are both compromised. All of these leading to food shortage, poor human health, severe ecological disorder and economical losses.

1.2 Nitrogen release and loss mechanism

Nitrogen is a primary nutrient for plant. Though it is abundantly present as a part of air in diatomic form (N_2), but in this form it is very stable and not accessible for plants. Plant can uptake nitrogen in the form of NH_4^+ and NO_3^-. Highly reactive and water soluble synthetic nitrogen based fertilizers like urea are thus prepared and applied to plants and relied upon as primary source of nitrogen. These fertilizers bring significant benefits but has other ecological effects along. Urea undergoes following physical and chemical transformation when applied to soil:

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

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

$$2NH_4{}^+ + 3O_2 \xrightarrow{Nitrosonomas\ ,Nitrosococus\ bacteria} 2NO_2{}^- + 2H_2O + 4H^+ + Energy$$

$$2NO_2{}^- + O_2 \xrightarrow{Nitrobacter\ bacterium\ (nitrification)} 2NO_3{}^- + Energy$$

$$NO_3{}^- \xrightarrow{Microorganism\ ,\ O_2\ deficient\ soil} N_2 + N_2O$$

$$NH_4{}^+ \xrightarrow{Urease\ enzyme\ ,\ \ Basic\ soil\ pH} NH_3 + H^-$$

Once urea is applied, urease enzyme and moisture convert it to ammonium (NH_4^+), carbondioxide and ammonia. Ammonium (NH_4^+) is oxidized to NO_2^- in presence of nitrite bacteria is further easily oxidized to NO_3^- by nitrified bacteria. At high soil pH > 7, ammonium (NH_4^+) converts to ammonia (NH_3) and escape into atmosphere while at pH < 7, ammonium (NH_4^+) is turned to nitrate (NO_3^-). This nitrate (NO_3^-) is absorbed by plant but if NO_3^- is present in high concentration, it can be leached out to ground water while remaining NO_3^- is denitrified into N_2O, N_2 and NO which are released to atmosphere. The production of nitric oxide (NO) and nitrous oxide (N_2O) gases contributes to greenhouse effect and has negative effect on the atmosphere [9]. Ammonia volatilization and N_2O formation is directly associated to high concentration of ammonium (NH_4^+) and nitrate (NO_3^-) respectively. Reducing accumulation of ammonium (NH_4^+) and nitrate (NO_3^-) could increase nitrogen use efficiency and reduce losses [10].

It is essential to control nutrients release rate leading to increased nitrogen use efficiency and minimized losses to ensure lower negative impacts of nitrogenous fertilizers on environment.

1.3 Zinc importance

Zinc is essential for both plants and human beings. Deficiency of zinc in crops is a global micronutrient problem and may be responsible for reduction in yields of crops of up to 40% without showing symptoms of any disease. Zinc plays significant role in multiple enzymatic reactions, metabolic processes and capacity for nutrients and water uptake. High pH, organic matter and $CaCO_3$ contents can reduce availability of Zinc. Deficiency of zinc significantly affects the root development process of plants. Deficiency of zinc could lead to retarded growth, delayed maturity and reduced yield. Zinc affects the uptake of nutrients and water and its deficiency could reduce growth and yield significantly. Almost all crops shows positive response to Zinc application [4].

Zinc deficiency along with Vitamin A deficiency is stated as the biggest problem of world by eight economist including five Noble laureates at Copenhagen consensus (www.copenhagenconsenses.com). In humans, zinc is essential for more than 300 enzymes and vital in improvement of immune system and growth activation (height, body and weight). Zinc helps human protect against infectious diseases and face psychological stress. Deficiency of zinc in humans, especially in children could lead to dwarfism, weak immune system, infections and death [11]. In infants and children, zinc deficiency could lead to pneumonia and diarrhea [12] which according to UNICEF (2012) contributes to 18% and 15% of the global death in children under age five years. In children most of deaths due to pnuemania and diarrhea could be prevented (UNICEF 2012)

1.4 Slow Release Urea Fertilizers

Solubility of urea is the most important property governing the losses from conventional urea. Slow release urea fertilizer are created with an aim to provide nutrients to plants according to their needs. This can be achieved by coating urea with low solubility or membrane layer forming polymers and bio-inhibitors. Controlling or slowing down the release rate of urea can increase the efficiency of urea [13]. It has many benefits i.e. reduced fertilizer losses, sustainable nutrient supply, lowered application frequency and reduced negative effects of overdosage.

1.5 Zinc coated urea fertilizers

To overcome zinc deficiency, different chemical forms of zinc i.e. Zinc sulphate ($ZnSO_4$) in form of monohydrate and heptahydrate, Zinc oxide (ZnO), Zin nitrate ($Zn(NO_3)_2$), Zinc carbonate ($ZnCO_3$), and Zinc chloride ($ZnCl_2$) have been used. All of these vary in terms of zinc content, effectiveness and cost for different types of different types of soils. These zinc based chemicals are altered to form which is highly available to crops for sustained growth. Zinc coated urea provides micronutrient Zinc efficiently to soil and leads to zinc rich crop. With high degree of correlation between zinc deficiency in human to soil and plant, overall health of developing countries will also improve. Most of the urease inhibitors being phyto-toxic and banned in majority of the world, micronutrients like Zinc are reported to act as a urease inhibitor [14]. Zinc effectively reduce volatilization losses through urease inhibition [15].

Chapter 2

Literature Review

Much research has been carried out on idea of development and production of “smart fertilizers” forming the basis for stable fertilizer market in order to reduce costs, environmental affects and maximize profits. Coating of urea with micronutrients and control release materials are the foundations for the processes leading to significant changes in fertilizer world with idea of smart fertilizers. Methods to control release rate involved coating urea with semi permeable layers, bio inhibitors i.e. urease and nitrification inhibitors. Bio inhibitors inhibits urease soil enzyme activities and causes urea to not breakdown easily. Micronutrients required by plants i.e. Zinc, boron, iron and copper are of substantial importance in increasing the nitrogen use efficiency and nutritional quality getting a lot of attention and popularity. Multiple materials as zinc sources are tested including Zinc sulphate hepta hydrate, Zinc sulphate monohydrate, Chelated Zinc (Zn-EDTA), nano and bulk zinc oxide.

2.1 Sulphur Coated Urea

Sulphur coating is economic and low in cost. It shows slowed but irregular release rate. Sulfur has been used as a coating substance since 1950’s to lower pH of alkaline soils and act as secondary nutrient.

Blouin et al. [16] in 1960’s synthesized slow release sulfur coated urea at pilot plant scale. The equipment used were spray machine, rolling drums and vacuum creating device. First urea was coated with wax which acted as a sealant and then sprayed with molten sulfur. Wax prevented solubility of urea in soil by occupying free spaces and pores.

Pooniya et al. [17] conducted field experiments on Sulphur coated urea with maize as test crop. On basis of average data of 2 years, an increase of 12.8% in yield and 16.7% in total nitrogen uptake was observed over uncoated urea.

2.2 Polymer Coated Urea

Polymer coated urea provides controlled release rate but is highly expensive. If polymer used is non degradable, it will pose as a pollutant threat. The membrane formed by polymer will initiate diffusion and penetration of water through barrier layer to fertilizer core. The next stage will be the swelling and increase of osmotic pressure inside fertilizer core. This swelling and increase of osmotic pressure will lead to concentration and pressure gradient and it would drive gradual diffusion of nutrients from fertilizer core. Much research has been carried out on different polymers as potential control release materials.

Ito et al. [18] used double coating with isobutylidendiurea as inner coating and used polyethylene glycol (PEG) and starch as outer coating materials. First coating layer with microchannels had a high diffusion rate in comparison to starch PEG layer. Higher starch content resulted in decreased release rate.

Perez et al. [19] coated ethyl cellulose using Fluidized bed coater on urea granules. Ethanol 5% solution was used. Ethyl cellulose displayed good film forming properties and lower toxicity with excellent physical and chemical resistance. Refractive index test was used to measure release rate. Ethyl cellulose showed good release results and reported a release time of 48h in comparison to 0.5h for unamended urea but relation of coating thickness to release rate was inverse. The complexity of process was main barrier in its commercialization.

S. Wu. et al. [20] synthesized polyurethane coated urea using rotary drum technique. Isocyanate and polyols were mixed to give polyurethane film and wax was used as a binder. Significant decrease in release rate was observed after fifty days soil incubation experiment.

Azeem et al. [21] used starch modified with polyvinyl alcohol as coating materials. Both are biodegradable, cheap and environmental friendly materials. Release time increased with increased coating thickness. It was concluded that uniform coating of significant thickness without coating imperfections can produce promising results.

Research on various other polymers were carried out and potential materials were tested including low density polyethylene (LDPE) [22], starch/acrylic acid [23], paraffin and polyethylene waxes [24] , polysulfone [25] , polyvinyl chloride [26] and polystyrene [27].

2.3 Sulphur Polymer Coated Urea

Sulphur alone has slow release affect but gives inconsistent results. Sulphur used in combination with polymer provides better sealing as compared to Sulphur alone. It shows slow and regular release rate but is relatively expensive [28]

2.4 Zinc Oxide Coated Urea

Both Zinc oxide nano particles and bulk forms are used as a micronutrient and applied either to soil directly or through coating urea. Milani et al. [29] study suggests that use of Zinc nano particle has very little advantage in terms of Zn dissolution and diffusion in soil over the Zinc bulk form.

Milani et al. [29] used Zinc oxide nano particles coated urea as a source of a zinc and macronutrient application to soil. Nano particles having greater reactivity and availability in comparison to bulk were investigated for potential zinc application source. When coated, Zn from Zinc oxide nano particles were not more diffusible or mobile in comparison to bulk forms of zinc oxide as it was anticipated.

Shivay et al. [30] used both Zinc oxide and Zinc sulphate heptahydrate as coating materials with different zinc percentages i.e. 0.5%, 1%, 1.5%, 2%. Field study was conducted using basmati rice as study crop. Zinc application increased the overall yields, Zinc uptake and concentrations in basmati rice. 2% Zinc sulphate heptahydrate was found as best sample very closely followed by 2% Zinc oxide sample.

Aziz et al. [31] investigated the effect of three different Zinc oxide nano particle application rates i.e. 1.4, 2.8 and 3.6 mg/kg soil along with Zeolite i.e. 141, 282 and 423 mg/kg soil and biogas slurry on Nitrogen and Zinc uptake and soil nutrient availability in a pot test. Zinc oxide nano particles and Zeolite significantly increased soil Nitrogen content. Co-mixing of Zinc oxide and zeolite in biogas slurry made no difference on Nitrogen uptake but significantly increased Zinc uptake. The treatments did not increase electrical conductivity or pH of soil in comparison to control.

2.5 Zinc Sulphate Coated Urea

Vijay et al. [17] synthesized 2.5% Zinc coated urea using Zinc sulphate hepta hydrate and gum acacia as binder. On the basis of results of 2 years with maize as test crop, yields were increased by 9.9% over prilled urea. Total Nitrogen uptake was increased by 17.1% while Zinc uptake was increased by 32.4% over conventional urea.

Nasima et al. [14] used micronutrients zinc and copper sulphate as urease inhibitors for coating of urea. Other materials i.e. agar, gelatin and palm stearin were used as adhesive agents. Coating materials did not show significant differences in chemical and physical properties of urea. It was concluded from the study that these coating materials had no severe or adverse effects on urea properties. Further field test was conducted with guinea grass as test crop [32]. All the treatment had significant advantages in yield, nitrogen, copper and zinc uptake over uncoated urea.

Chapter 3

Aim of Project

The aim of the study was to create single fertilizer with urea as base material which is inexpensive, more efficient than conventional urea and has micronutrient Zinc along with primary nutrient nitrogen. Incorporating micronutrient to urea will not only make it convenient for farmer in terms of single application requirement but also will ensure better field distribution. It will ensure zinc application automatically , improve crop productivity and nutrition quality of crops. The aims were extended to create fertilizer that is easy to manufacture and does not require existing process alteration and organic solvent. Above all the fertilizer should be biodegradable to not pose any environmental concern. Further hypothesis was that it should not have adverse effects on properties of soil.

3.1 Objectives

1. Synthesis of zinc coated urea fertilizers
2. Characterization of zinc coated urea fertilizers
3. Analyze effect on plant shoots and roots
4. Analyze Zinc content in soil
5. Analyze effect on release rate

Chapter 4

Materials and Methods

In this chapter, materials used for coating and methodology of coating are discussed. Characterization tests along with pot tests are also discussed.

4.1 Materials

Prilled urea obtained from Fauji fertilizer Company Ltd Pakistan was sieved to obtain prills of uniform size approximately 2mm. All coating materials used i.e. Zinc sulfate heptahydrate, Zinc oxide, Gelatin, Paraffin oil were of analytically pure quality and were obtained from Daejung Korea. Molasses used in coating was obtained from a local sugar mill i.e. Al Moiz Sugar Mill, D.I. Khan Pakistan. Materials used in release test i.e. Hydrochloric acid, p-dimethyl amino benzaldehyde were also of analytical purity.

4.2 Synthesis of coating solution

All coating solutions were prepared in de-ionized water and constant stirring was employed without any heating. Composition for every treatment is given in **Table 4.1** All percentages are by weight.

Table 4.1: Urea Fertilizer Treatments

Urea treatment	**Zinc (%)**	**Molasses (ml)**	**Paraffin Oil (ml)**	**Gelatin (%)**
Urea (UC)	-	-	-	-
Zinc oxide coated urea (ZnO)	2.5	-	-	-
Zinc oxide sonicated coated urea (ZnO-Son)	2.5	-	-	-
Zinc oxide + Gelatin coated urea (ZnOG)	2.5	-	-	1.5
Gelatin coated urea (G)	-	-	-	1.5
Zinc oxide + Molasses + Paraffin oil coated urea (ZnOM)	2.5	6	3	-
Zinc sulphate hepta hydrate + Molasses + paraffin oil coated urea (ZnSM)	2.5	6	3	-

Zinc sulphate hepta hydrate coated urea (ZnS)	2.5	-	-	-

All the samples contained 2.5% Zn by weight apart from gelatin coated urea sample (G) and uncoated urea (UC). Gelatin, molasses and paraffin oil were used as additives in different combinations. Solution for ZnO-Son sample was sonicated for uniform suspension and good dispersion. In total 4 samples were prepared using Zinc oxide, 4 using Zinc sulphate heptahydrate and 1 using Gelatin only.

4.3 Coating Methodology

Coating for all treatments were carried out in YX-1000 mini Fluidized spray granulator developed by Shanghai Pilotech Instrument and Equipment Company Ltd. Apparatus was made of stainless steel (SUS 304) and bosiloricate glass was used for monitoring the coating process. Urea prills were introduced at middle of bed and spray nozzle located at bottom was used to spray the coating solution. A peristaltic pump was used for movement of coating solution from container to nozzle head. Coating solution was atomized with pressurized air from compressor. Hot air was introduced from the bottom and kept the bed fluidized at all times. At one time 500 gram batch was run. To prevent prills agglomeration and ultimately bed collapse, intermittent coating was conducted rather than continuous. Coating process was started once steady temperature 80 C was achieved and final product was dried till after 15 minutes of coating process to completely dry product. After completion, coated urea treatments were taken out from bed and were tested using different characterization techniques and pot tests.

4.4 Pots preparation and treatment application

Pots were prepared and study was carried out at a research site of PMAS Arid Agriculture University, Rawalpindi (33.6492°N, 73.0815°E, 508 m above sea level) from the month of December to June. Rye grass was used as a test crop to determine affect of different treatments on it. Soil used for carrying out study was Clay loam soil which was also used in study by [33]. The temperature in the winter months remained low i.e. from 2 °C to 25 °C and in summer months it reached upto 40 °C. Total of 9 treatments were subjected to testing that are Untreated control (C), Uncoated urea

(UC), Zinc oxide-coated (ZnO), Zinc oxide sonicated-coated (ZnO-Son), Zinc oxide with Gelatin-coated (ZnOG), Gelatin-coated (G), Zinc oxide with Molasses-coated (ZnOM), Zinc sulphate with molasses-coated (ZnSM) and Zinc sulphate-coated (ZnS). For every sample there were three treatments with two repetitions. Soil samples and harvesting was carried out two times during the whole cycle.

Figure 4.1: Pots Preparation

Each plastic made pot with a diameter of 26 cm and area of 0.053 m^2 was filled with 18 kg of soil and Nitrogen was applied at the rate of 270 Kg N ha^{-1}. The soil was sieved through 2 mm mesh before use to remove any root debris or solid aggregate particles. Treatments were applied to the soil and 0.3 g of Rye grass seeds were sown in each pot. The pots were arranged in manner of completely randomized design (CRD) to ensure natural conditions for each pot sample to grow. All the pots were maintained with water at 60% of holding capacity to keep them moisturized and were regularly watered manually whenever required.

4.5 Physical and Chemical Analysis of coated urea

The uncoated and coated urea samples were analyzed using SEM, FTIR, XRD, UV-Vis Spectrophotometer and Universal testing machine (UTM). SEM was used to study morphology. FTIR and XRD was used to examine interaction nature of materials and verify zinc presence respectively. Release rate was measured using UV-Vis and crushing strength was determined using UTM.

4.5.1 Scanning electron microscopy (SEM)

The surface morphology and micro structure of all the samples were examined utilizing Hitachi S-4700 scanning electron microscope. Gold sputtering was carried out on all samples before analysis. Magnification range employed was from 25 to 2000x and applied acceleration voltage was 20 kV.

4.5.2 Fourier transform infrared spectroscopy (FTIR)

The interaction between urea and coating materials were analyzed using Perkins Elmer Spectrum 100 Fourier transform infrared spectroscope. Pellets for all samples were prepared by crushing samples and mixing with potassium bromide. The wavelength for analysis was in range of 400 to 4000 cm^{-1}.

4.5.3 X-Ray Diffraction (XRD)

Presence of zinc was verified and crystallinity was studied by XRD characterization using X-Ray JSX 3201, JEOL, Japan (40 mA). Scan angle was varied from 10 to 70 while the step size used was 0.04 with 1 sec counting time per step. Cu K α-1 radiation was used for the analysis [34].

4.5.4 Dissolution rate of N from Gelatin coated fertilizer

Release rate for gelatin coated urea acting as barrier to diffusion was determined by P-methyl Amino Benzaldehyde method using GENESYS 20 UV-visible spectrophotometer and compared to uncoated urea. Solutions with known concentrations i.e. 20 ppm, 40 ppm, 60 ppm, 80 ppm, 100 ppm were prepared and absorbance was determined from them using spectrophotometer. Calibration curve was drawn by plotting graph between concentration and absorbance. Slope and y intercept was determined to form equation for calculation of concentration from absorbance value.

Table 4.2: Absorbance for Urea concentrations

Sr. no.	Concentration (ppm)	Absorbance (Au)
1	0	0.0318
2	20	0.0351
3	40	0.0428
4	60	0.0457
5	80	0.0495
6	100	0.0579

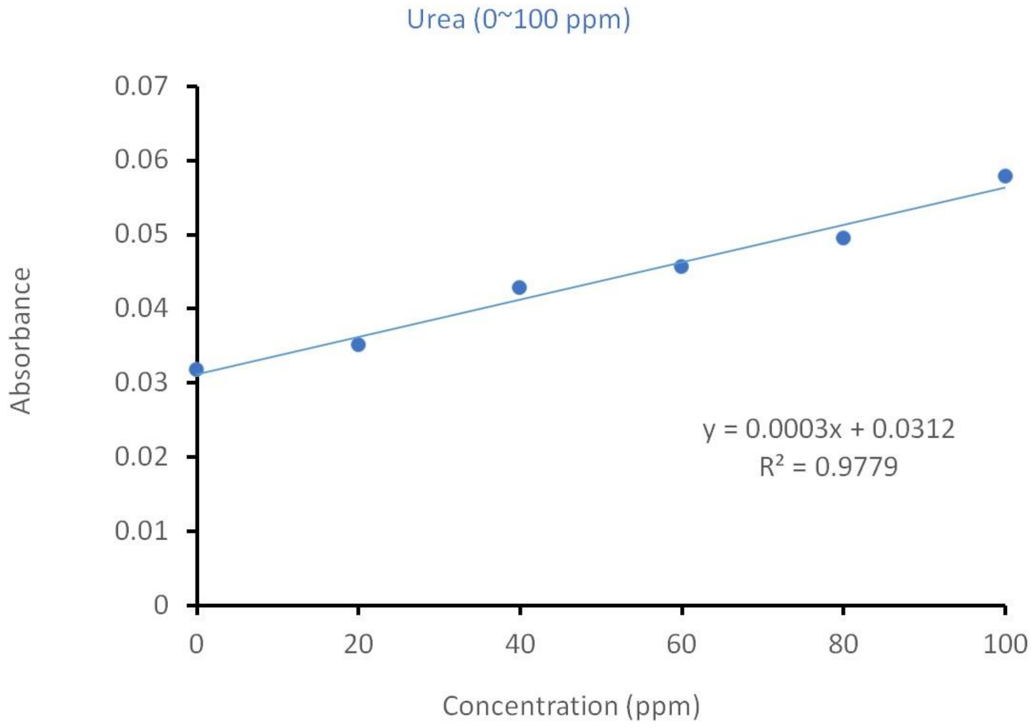


Figure 4.2: Calibration Curve

4.5.4.a Test Protocol

A 5 Liters glass jar was filled with water and 10 grams of urea sample was immersed in it. A sample aliquot of 10 ml was taken from the middle of the beaker after different time intervals i.e. 3 mins, 6 mins, 9 mins, 12 mins, 15 mins, 30 mins, 60 mins. This 10 ml sample aliquot was diluted up till 50 ml and stirred. After stirring, 10 ml is taken from this 50 ml sample. 1 ml of HCl (1:1) and 5 ml p-dimethyl amino benzaldehyde is then added to the 10 ml and further water is added to the sample to make it 50 ml in total. Finally absorbance for this sample is determined at wavelength of 418 nm. That absorbance value is then used to calculate the concentration through equation formed using the calibration curve. The coefficient of determination (R2) was 0.9779.

$$Urea\ (ppm) = \frac{Absorbance - Y\ intercept}{Slope}$$

$$Urea\ (ppm) = 3333.3 \times Absorbance - 104$$

4.5.5 Crushing Strength

Crushing strength test was carried out to make sure if the samples prepared could withstand the physical impacts of different supply chain operations from manufacturing to the market without getting fractured. Crushing strength was determined by applying increasing pressure to every urea sample prill using Universal testing machine (AGX Plus) until the prill was crushed. At this point, the compressive force was recorded.

4.6 Plant Analysis

Grass was harvested two times during the cycle first after 109 days and for the second time after 177 days of seed sowing. After final harvest, roots were also taken out and placed in cold water along with soil clump. After keeping it soaked for 2 hours, roots parts were placed in 0.5 mm mesh and put under high speed tap water to separate soil from it Following parameters were determined after the harvests

1. Plant Height
2. Fresh Matter Yield
3. Dry Matter Yield
4. Plant Nitrogen Uptake
5. Plant Zinc Uptake

4.6.1 Plant Height

Before harvesting the height of plant was measured using meter rod. For each pot, height was measured at three different points.

4.6.2 Fresh Matter Yield

After harvesting, fresh weight for both roots and shoots were measured. The shoots or stems were cut and weight balance was used to measure fresh weight in grams.

4.6.3 Dry Matter Yield

To determine the dry matter yield, the shoots and roots harvested were dried in an oven at temperature of 70 °C for 48 hours. After drying, weight for both shoots and roots were measured using a weight balance [35].

4.6.4 Plant N uptake

Nitrogen content in the plant was determined using Kjeldahl method. 5 gram of grinded dry plant powder was added to the digestion tube. 3.5 gram of digestion catalyst mixture and 10 ml of concentrated sulphuric acid (H_2SO_4) were added into digestion tube and swirled. The mixture was heated for at least 3 hours at temperature of 420 °C. Finally solvated ammonium ions were captured using distillation with the help of 40% sodium hydroxide (NaOH) solution and boric acid (H_3BO_3). Titration was carried out using 0.01 M H_2SO_4.

Using the Nitrogen uptake value, Apparent Nitrogen Recovery (ANR) for coated samples was also calculated as follows:

$$ANR(\%) = \frac{(N\ uptake\ in\ urea\ treated\ pot - N\ uptake\ in\ control\ pot)}{Amount\ of\ N\ applied} \times 100$$

4.6.5 Plant Zn uptake

Zinc content in shoots and roots for plant was determined using wet digestion technique (di-acid digestion) procedure on an atomic absorption spectrophotometer (prasad et al., 2006) Using the Zinc uptake value, Apparent Zinc Recovery (AZnR) for Zinc coated samples was also calculated as follows:

$$AZnR(\%) = \frac{(Zn\ uptake\ in\ Zn\ treated\ pot - Zn\ uptake\ in\ control\ pot)}{Amount\ of\ Zn\ applied} \times 100$$

4.7 Soil Zn Analysis

The samples of soil for all treatments were collected three times. First sample was taken before applying any fertilizer, second sample after first harvest and third sample after final harvest. A hand auger was used to get the sample from each pot from three different locations. These different samples from same pot were then mixed and were tested. The zinc content of soil was extracted using di-acid method and analyzed using Atomic absorption spectroscopy [36].

4.8 Statistical Analysis

The experimental data from pot tests were statistically analyzed using analysis of variance (ANOVA) to determine the impact of coated fertilizers and how significantly treatments were different from each other. Based on differences homogenous groups were assigned to each treatment. When significant difference was detected by F-test, mean comparisons were made using LSD test at probability of 5%. The tests were performed using statistical software package SPSS Statistics 17.0 (IBM New York USA).

Chapter 5

Results and Discussions

5.1 Plant Analysis

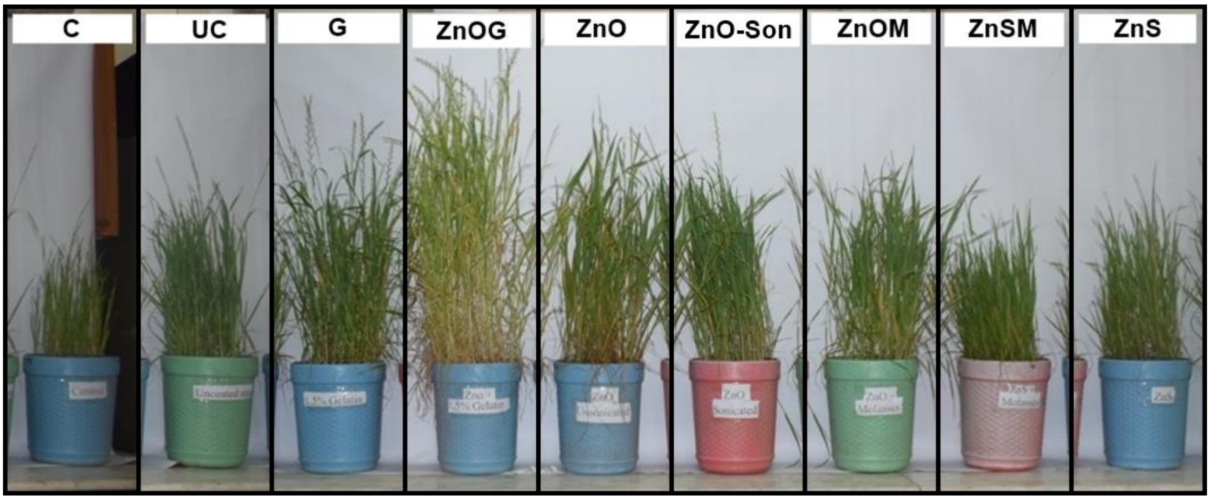


Figure 5.1: Plants before first harvest

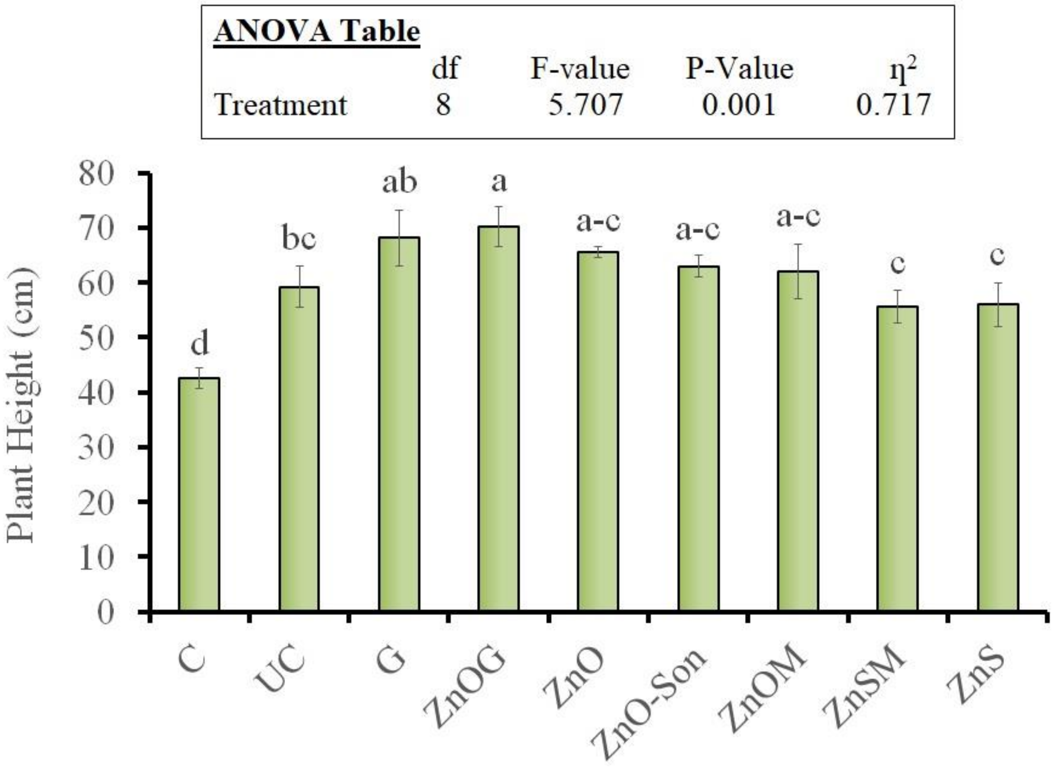
Figure 5.1 shows the plants before harvesting. ZnOG was the best sample visually followed by G and both are significantly better than uncoated urea and control sample.

5.1.1 Plant Height

Plant height was recorded one time before 1st harvest at maturity of plant and is shown in **Table 5.1** and **Figure 5.2**. As per the heights recorded, maximum plant height was recorded for ZnOG (70.11±3.67 cm) closely followed by G (68.11±5.06 cm). The height for uncoated urea was recorded as 59.16 cm whereas minimum plant height was recorded for C sample (42.5±1.85 cm). Plant height was significantly improved with ZnOG and G samples. Results for all Zinc oxide coated samples were promising and were statistically different from uncoated and control samples. Zinc sulphate coated samples were almost similar in results to uncoated urea with no benefits over it.

Table 5.1: Plant Height

Treatment	Mean Plant Height (cm)	SE
C	42.5	1.855921
UC	59.1666667	3.785939
G	68.1111111	5.061047
ZnOG	70.1111111	3.674655
ZnO	65.5	0.976578
ZnO-Son	62.9444444	1.946824
ZnOM	62.0555556	4.98733
ZnSM	55.6111111	3.015904
ZnS	55.9444444	4.038396



ANOVA Table

	df	F-value	P-Value	η^2
Treatment	8	5.707	0.001	0.717

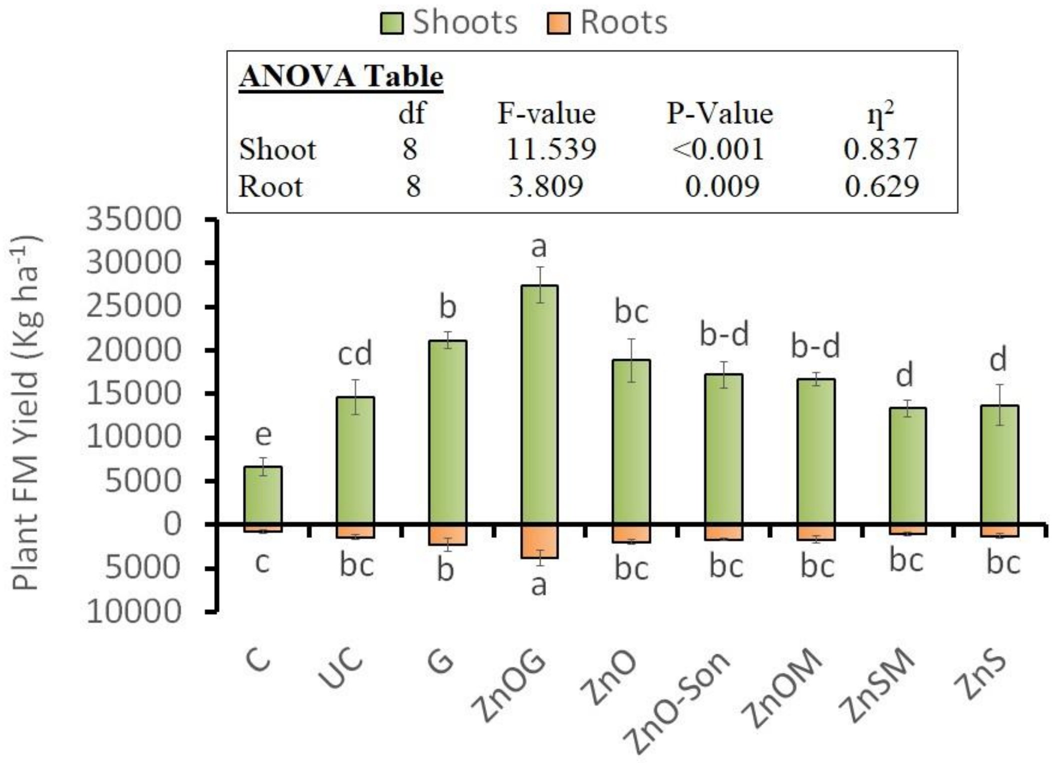
Figure 5.2: Plant Height

5.1.2 Plant Fresh Matter Yield

Plant Fresh Matter Yields was recorded for both shoots and roots for all samples and are shown in **Table 5.2** and **Figure 5.3**. The maximum fresh matter yield for shoots and roots was recorded for ZnOG sample (27491 kg/ha and 3833 kg/ha respectively) closely followed by G sample (21130 kg/ha and 2293 kg/ha respectively) . Shoots and Roots fresh matter yield recorded for uncoated urea was 14635 kg/ha and 1394 kg/ha respectively whereas minimum shoot and root fresh matter yield was recorded for C sample (6656 kg/ha and 823 kg/ha respectively). Fresh matter yields were significantly increased with ZnOG and G samples. All the Zinc oxide coated samples showed superior yield as compared to un coated urea showing benefits. Zinc sulphate coated samples were statistically identical to un amended area and not showed promising results.

Table 5.2: Plant Fresh Matter Yield

Treatment	Shoot Fresh Matter Yield (Kg/ha)	Root Fresh Matter Yield (Kg/ha)
C	6656 ± 1009	823 ± 221
UC	14635 ± 2018	1394 ± 224
G	21130 ± 979	2293 ± 812
ZnOG	27491 ± 2044	3833 ± 881
ZnO	18856 ± 2513	1944 ± 237
ZnO-Son	17203 ± 1527	1703 ± 136
ZnOM	16716 ± 785	1685 ± 368
ZnSM	13370 ± 960	1090 ± 223
ZnS	13714 ± 2352	1284 ± 261



ANOVA Table

	df	F-value	P-Value	η^2
Shoot	8	11.539	<0.001	0.837
Root	8	3.809	0.009	0.629

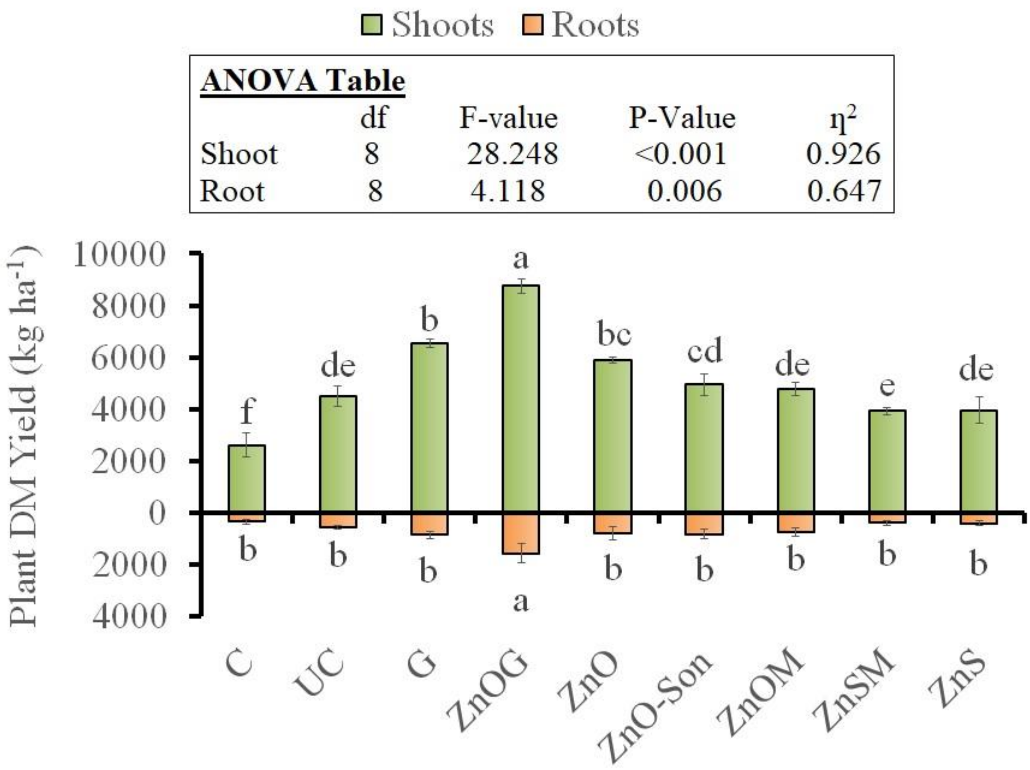
Figure 5.3: Plant Fresh Matter Yield

5.1.3 Plant Dry Matter Yield

Plant Dry Matter Yield was recorded for both shoots and roots for all samples and are shown in **Table 5.3** and **Figure 5.4**. The maximum dry matter yield for shoots and roots was recorded for ZnOG sample (8746.23 kg/ha and 1580 kg/ha respectively) closely followed by G sample (6530.26 kg/ha and 861 kg/ha respectively) . Shoots and Roots dry matter yield recorded for uncoated urea was 4501 kg/ha and 576 kg/ha respectively whereas minimum shoot and root dry matter yield was recorded for C sample (2601.57 kg/ha and 350 kg/ha respectively). Dry matter yields were significantly increased with ZnOG and G samples. All the Zinc oxide coated samples showed superior yield as compared to un coated urea showing benefits. Zinc sulphate coated samples were statistically identical to un amended area and not showed promising results.

Table 5.3: Plant Dry Matter Yield

Treatment	Shoot Dry Matter Yield (Kg/ha)	Root Dry Matter Yield (Kg/ha)
C	2601.571631 ± 457.93	350 ± 88
UC	4501.522421 ± 401.97	576 ± 64
G	6530.263886 ± 149.75	861 ± 135
ZnOG	8746.232392 ± 278.35	1580 ± 368
ZnO	5884.388264 ± 130.94	792 ± 269
ZnO-Son	4948.25306 ± 425.05	830 ± 187
ZnOM	4771.021714 ± 269.29	760 ± 154
ZnSM	3921.77216 ± 148.5	403 ± 81
ZnS	3957.910439 ± 498.46	412 ± 76



ANOVA Table	df	F-value	P-Value	η²
Shoot	8	28.248	<0.001	0.926
Root	8	4.118	0.006	0.647

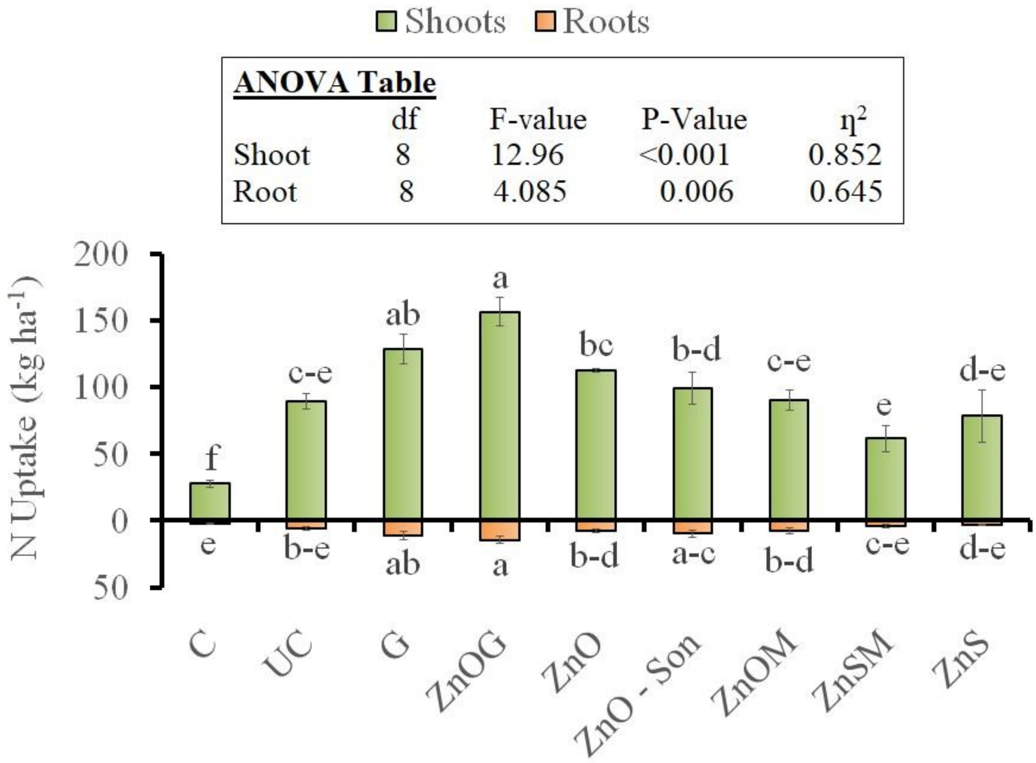
Figure 5.4: Plant Dry Matter Yield

5.1.4 Plant N uptake

Plant Nitrogen uptake was determined for both shoots and roots for all samples and are shown in **Table 5.4** and **Figure 5.5**. The maximum nitrogen uptake for shoots and roots was recorded for ZnOG sample (156.25 kg/ha and 14.5 kg/ha respectively) closely followed by G sample (128.25 kg/ha and 11 kg/ha respectively) . Shoots and Roots nitrogen uptake determined for uncoated urea was 89.21 kg/ha and 6.08 kg/ha respectively whereas minimum shoot and root nitrogen uptake was recorded for C sample (27.47 kg/ha and 1.94 kg/ha). Nitrogen uptake was significantly increased with ZnOG and G samples. All the Zinc oxide coated samples had improved the Nitrogen uptake over uncoated urea and were statistically different and better. Zinc sulphate coated samples had negative effect on nitrogen uptake and nitrogen uptake was less than uncoated urea sample for them.

Table 5.4: Plant N uptake

Treatment	Shoot N uptake (Kg/ha)	Root N uptake (Kg/ha)
C	27.47434343 ± 2.67	1.945057667 ± 0.22
UC	89.21568542 ± 6.18	6.088913637 ± 1.36
G	128.2513985 ± 11.37	11.00260749 ± 3.07
ZnOG	156.2546097 ± 10.71	14.49057192 ± 2.99
ZnO	112.7829088 ± 1.38	7.880176047 ± 1.39
ZnO-Son	99.284047 ± 12.19	9.892653765 ± 2.89
ZnOM	90.24827407 ± 7.25	7.770322292 ± 2.22
ZnSM	61.33682273 ± 9.92	4.196413453 ± 1.31
ZnS	78.21893245 ± 19.52	3.569600849 ± 0.54


ANOVA Table

	df	F-value	P-Value	η^2
Shoot	8	12.96	<0.001	0.852
Root	8	4.085	0.006	0.645

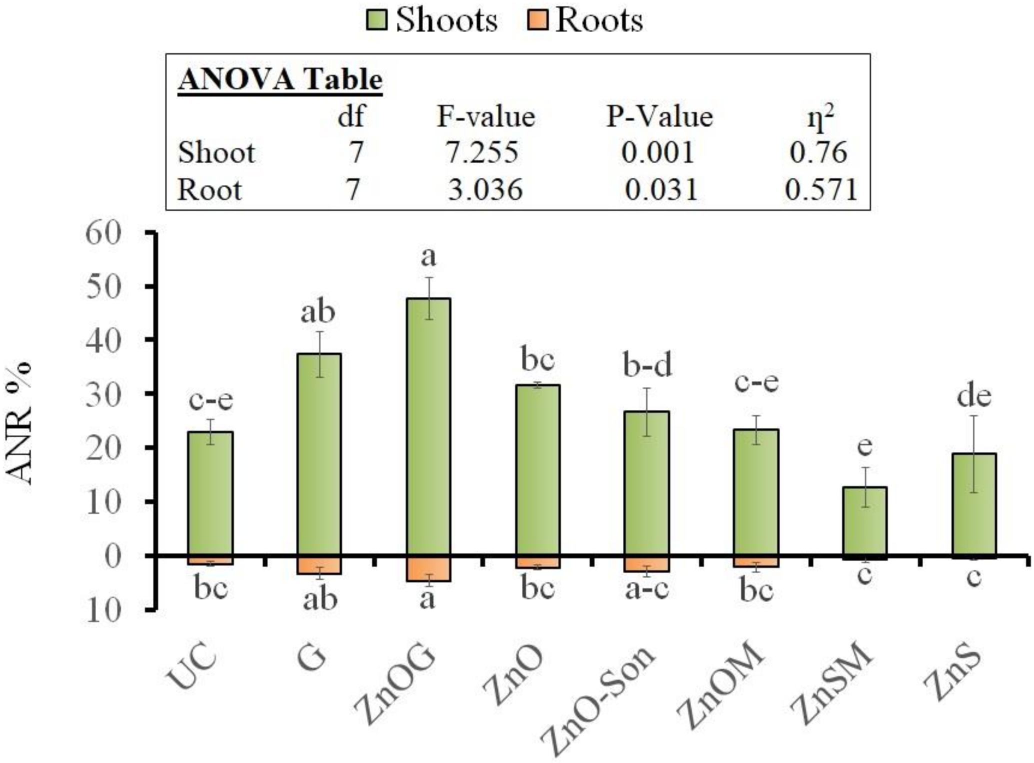
Figure 5.5: Plant N uptake

5.1.5 Plant Apparent Nitrogen Recovery (ANR)

Apparent Nitrogen Recovery is used as a measure of the nitrogen use efficiency. Based on Nitrogen uptake, ANR was calculated for shoots and roots of all samples and is shown in **Table *5.5*** and **Figure 5.6**. The maximum apparent nitrogen recovery for shoot and root was determined for ZnOG sample (48% and 4.6% respectively) followed by G sample (37% and 3.4% respectively). The shoots and roots ANR determined for uncoated urea was 23% and 1.5% respectively. The minimum shoot ANR was determined for ZnSM sample (13%) and minimum root ANR was determined for ZnS (0.6%). Apparent nitrogen recovery was significantly increased for ZnOG and G samples over un amended urea by 25% (more than doubled) and 14% respectively for shoots. All the Zinc oxide coated samples had improved ANR then amended urea for shoots and roots. However in case of Zinc sulphate, ANR was reduced than un coated urea and coating had affected the efficiency negatively.

Table 5.5: Plant ANR

Treatment	Shoot ANR (%)	Root ANR (%)
UC	23 ± 2	1.5 ± 0.5
G	37 ± 4	3.4 ± 1.1
ZnOG	48 ± 4	4.6 ± 1.1
ZnO	32 ± 1	2.2 ± 0.5
ZnO-Son	27 ± 5	2.9 ± 1.1
ZnOM	23 ± 3	2.2 ± 0.8
ZnSM	13 ± 4	0.8 ± 0.5
ZnS	19 ± 7	0.6 ± 0.2



ANOVA Table

	df	F-value	P-Value	η^2
Shoot	7	7.255	0.001	0.76
Root	7	3.036	0.031	0.571

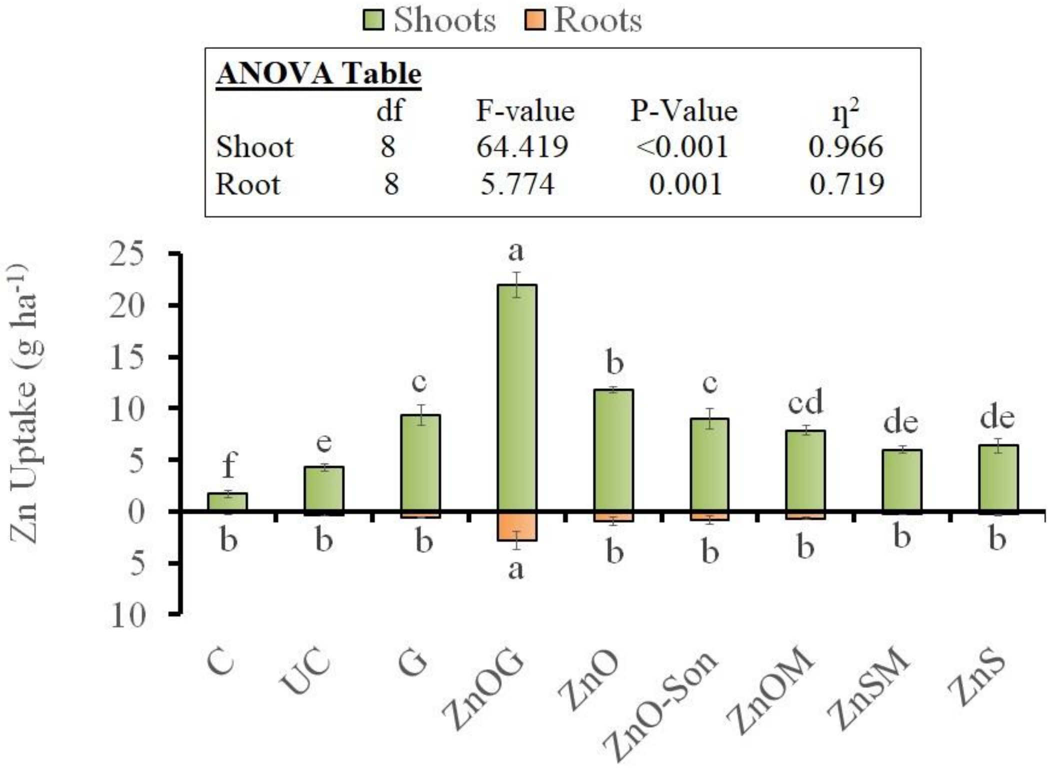
Figure 5.6: Plant ANR

5.1.6 Plant Zn uptake

Plant Zinc uptake was determined for both shoots and roots for all samples and are shown in **Table *5.6*** and **Figure 5.7**. The maximum zinc uptake for shoots and roots was recorded for ZnOG sample (21.98 g/ha and 2.83 g/ha respectively) and it was significantly different from other samples and no sample was close to it. Shoots and Roots zinc uptake determined for uncoated urea was 4.25 g/ha and 0.33 g/ha respectively whereas minimum shoot and root nitrogen uptake was recorded for C sample (1.67 g/ha and 0.18 g/ha). Zinc uptake was significantly increased with ZnOG samples. All the Zinc coated samples improved the Zinc content in shoots and roots and were statistically better than un coated urea. Zinc oxide coated samples showed better results than Zinc sulphate coated samples

Table 5.6: Plant Zn uptake

Treatment	Shoot Zn uptake (g/ha)	Root Zn uptake (g/ha)
C	1.678 ± 0.371	0.186 ± 0.049
UC	4.258 ± 0.323	0.337 ± 0.101
G	9.339 ± 1.006	0.603 ± 0.070
ZnOG	21.982 ± 1.191	2.836 ± 0.848
ZnO	11.771 ± 0.253	0.974 ± 0.376
ZnO-Son	9.002 ± 0.982	0.880 ± 0.420
ZnOM	7.845 ± 0.487	0.662 ± 0.145
ZnSM	5.976 ± 0.353	0.292 ± 0.047
ZnS	6.374 ± 0.728	0.295 ± 0.024



ANOVA Table

	df	F-value	P-Value	η²
Shoot	8	64.419	<0.001	0.966
Root	8	5.774	0.001	0.719

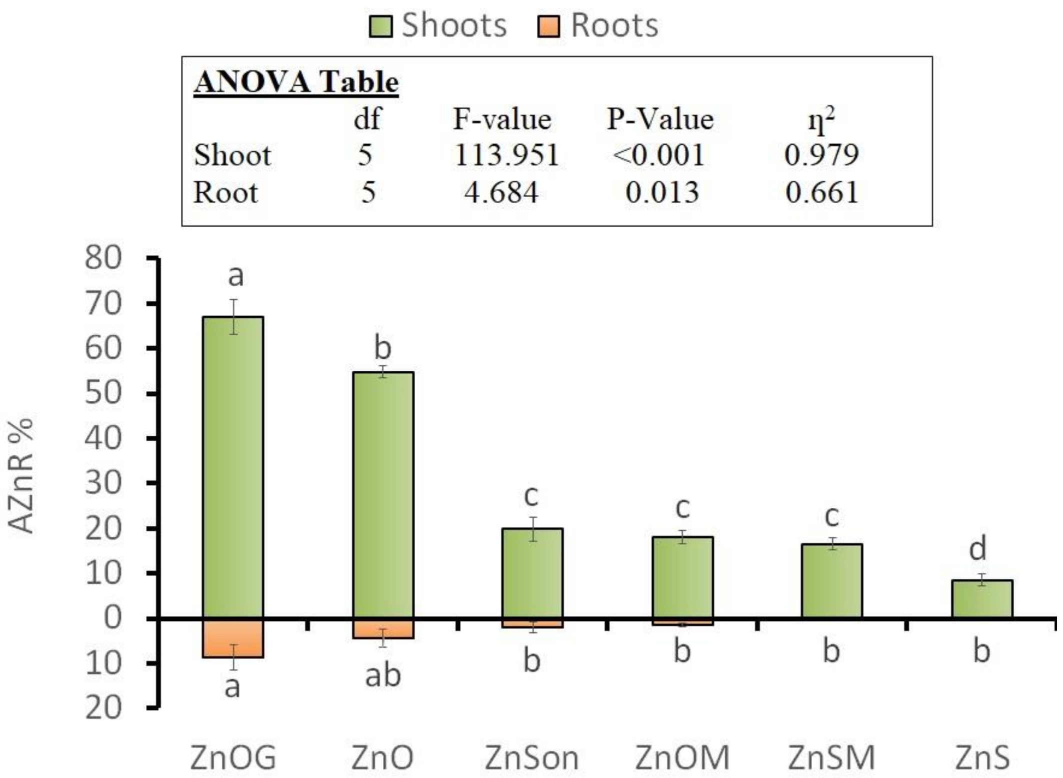
Figure 5.7: Plant Zn uptake

5.1.7 Plant Apparent Zinc Recovery (AZnR)

Apparent Zinc Recovery is used as a measure of the zinc use efficiency. Based on Zinc uptake, AZnR was calculated for shoots and roots of all samples and is shown in **Table 5.7** and **Figure 5.8**. The maximum apparent zinc recovery for shoot and root was determined for ZnOG sample (67% and 8.75% respectively) followed by ZnO sample (54.78% and 4.28% respectively). The minimum shoot and root AZnR was determined for ZnS sample (8.56% and 0.2% respectively).

Table 5.7: Plant AZnR

Treatment	Shoot ANR (%)	Root ANR (%)
ZnOG	67 ± 4	8.75 ± 2.79
ZnO	54.78 ± 1.37	4.28 ± 2.04
ZnO-Son	19.91 ± 2.67	1.88 ± 1.14
ZnOM	18.08 ± 1.43	1.39 ± 0.42
ZnSM	16.54 ± 1.36	0.4 ± 0.18
ZnS	8.56 ± 1.32	0.2 ± 0.04



ANOVA Table

	df	F-value	P-Value	η^2
Shoot	5	113.951	<0.001	0.979
Root	5	4.684	0.013	0.661

Figure 5.8: Plant AZnR

5.2 Soil Zn Analysis

Zinc content in soil for all samples was determined at three intervals i.e. before application, first harvest and final harvest and is shown in **Table 5.8** and **Figure 5.9**. Initially before application of fertilizer the zinc content of soil was 3.34 kg/ha. After 109 days of application of fertilizer and absorption by plant, the zinc content of soil for control (C) and un coated urea (UC) reduced to 2.09 kg/ha and 2.4 kg/ha respectively. For Gelatin coated urea (G), the zinc content of soil also reduced to 2.9 kg/ha. For all zinc coated samples, the zinc content of soil increased from the initial zinc content of soil.

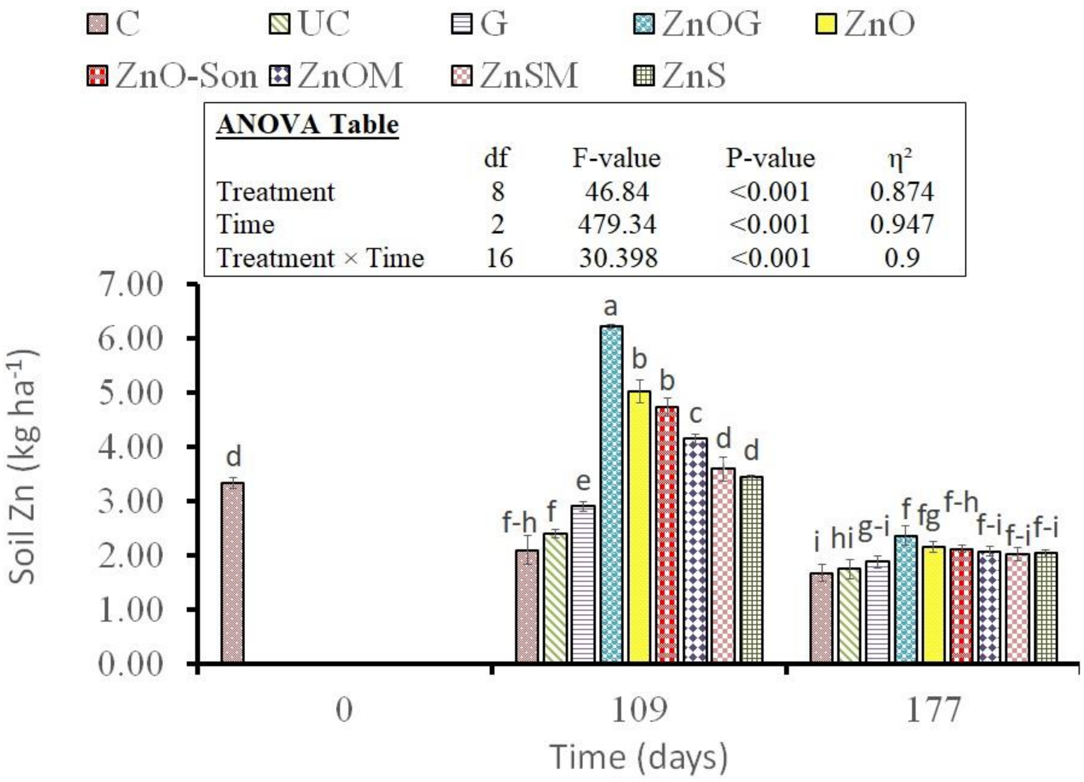
The maximum zinc content in soil after 109 days was recorded for ZnOG sample (6.22 kg/ha) followed by ZnO sample (5.02 kg/ha). This is in agreement with results of zinc uptake by plant where maximum zinc uptake were recorded for ZnOG and ZnO samples.

Similarly, after 177 days and final harvest of plants, the zinc content of soil was further reduced due to absorption by plant. Zinc content of soil for control (C) , uncoated (UC) and gelatin coated urea (G) reduced to 1.67, 1.74 and 1.88 kg/ha respectively.

After second harvest maximum zinc content in soil was recorded for ZnOG sample (2.36 kg/ha) closely followed by ZnO (2.16 kg/ha) and ZnO-Son (2.11 kg/ha) samples.

Table 5.8: Soil Zn content

Treatment	Day 109 (kg/ha)	Day 177 (kg/ha)
Initial	Day 0 = 3.34 ± 0.1 kg/ha	
C	2.09 ± 0.27	1.67 ± 0.15
UC	2.4 ± 0.07	1.74 ± 0.18
G	2.9 ± 0.09	1.88 ± 0.11
ZnOG	6.22 ± 0.03	2.36 ± 0.19
ZnO	5.02 ± 0.21	2.16 ± 0.1
ZnO-Son	4.73 ± 0.17	2.11 ± 0.07
ZnOM	4.14 ± 0.09	2.07 ± 0.09
ZnSM	3.59 ± 0.22	2.02 ± 0.13
ZnS	3.45 ± 0.03	2.04 ± 0.07



ANOVA Table

	df	F-value	P-value	η^2
Treatment	8	46.84	<0.001	0.874
Time	2	479.34	<0.001	0.947
Treatment × Time	16	30.398	<0.001	0.9

Figure 5.9: Soil Zn content

5.3 Effect of Gelatin coating on release rate of urea

Gelatin being a polymer is used as a slow release coating material to form a film over urea surface and control the release rate of urea. Both uncoated urea (UC) and gelatin coated urea (G) was tested for release rate to see and compare the effect of Gelatin on release rate of urea. **Figure 5.10** shows the release profile (percentage of Nitrogen added vs time) of uncoated urea and gelatin coated urea.

Table 5.9: Release rate of UC and G sample

Time (mins)	Uncoated Urea (% Release)	Gelatin coated Urea (% Release)
3	63.33	32.08
6	90.83	38.33
9	100	49.58
12	-	52.91
15	-	61.66
30	-	95.83
60	-	100

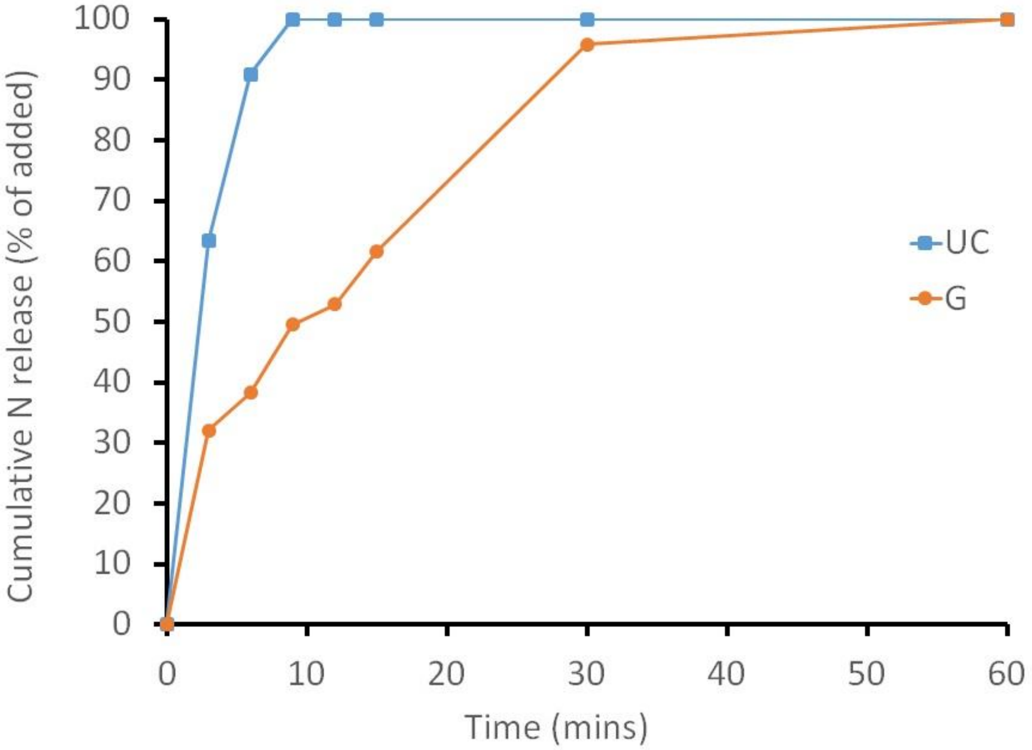


Figure 5.10: Release profile of UC and G sample

Uncoated urea releases nutrients quickly and is completely released between 6 and 9 minutes with 90% of nutrients released in 6 mins. With no coating barrier and high solubility of urea in water, the release occurs at very quick pace for un amended urea. Gelatin coating slows the release of urea to some extent with only 38% of nutrients released till 6 mins and follows a comparatively less steeper path by releasing nutrients over extended period till 30 mins at which 95% of nutrients were released. This is because of the obstruction film layer provided by gelatin coating. Gelatin being hydrophilic lets water penetrate through it and result in swelling of the coating layer with gradual release of nutrient through liquid bridges in swelled coating layer.

The results are in agreement with Literature [32] and results of pot tests. Gelatin coated samples i.e. ZnOG and G showed increase in efficiency (ANR%) by percentage of 25 and 14 respectively over uncoated urea. Gelatin improved the nitrogen use efficiency of urea and resulted in increased yields and Nitrogen uptake. As by results of pot tests, combining it with ZnO further improved the Nitrogen use efficiency and Nitrogen uptake due to urease inhibition effect of zinc.

5.4 Surface Morphology

The morphology and microstructure of all the samples were investigated using Scanning electron microscope. Coating surface was analyzed for uniformity, shape and structure of coating layer deposited on urea. **Figure *5.11*** shows the SEM images for all the samples.

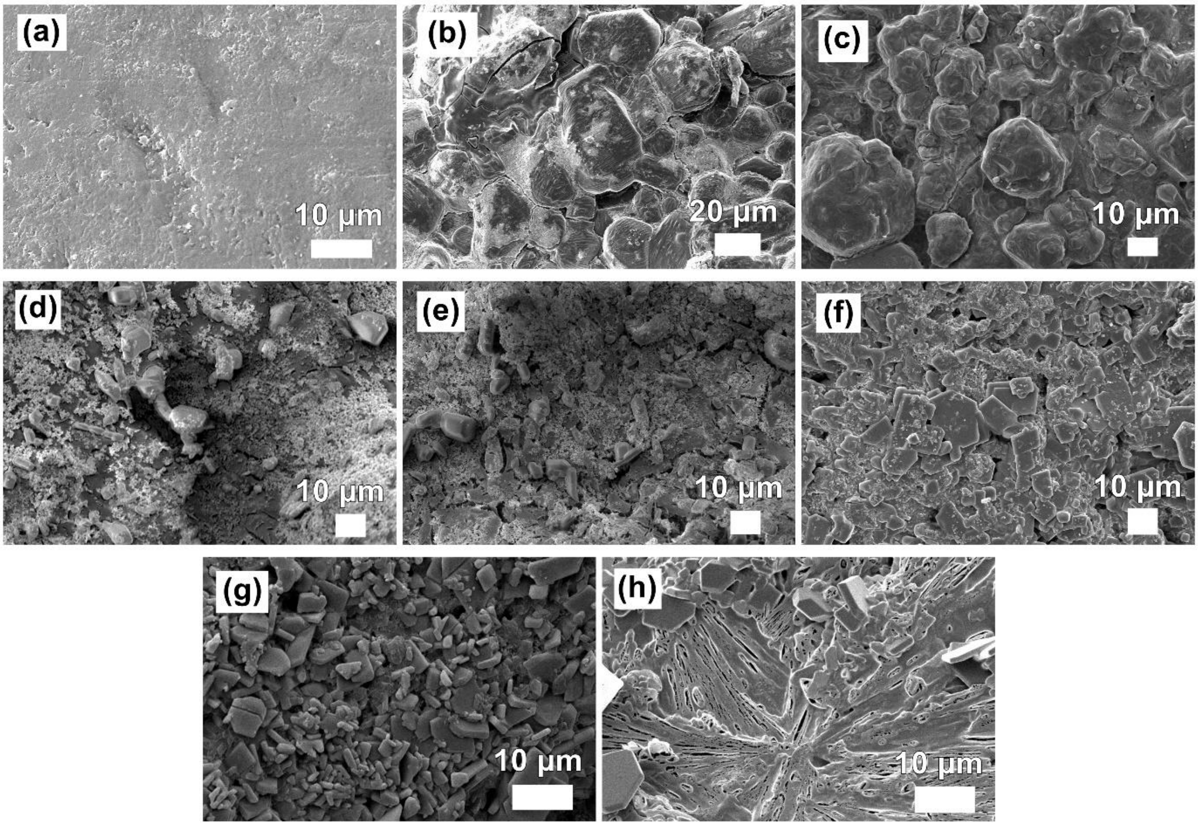


Figure 5.11: SEM images of fertilizer samples (a) UC, (b) ZnS, (c) ZnSM, (d) ZnO, (e) ZnO-Son, (f) ZnOM, (g) ZnOG, (h) G

The SEM images displayed significant differences in microstructure and morphology for different coated samples. Samples containing additives i.e. Molasses and Gelatin showed better uniformity in coating layer in comparison to samples containing only water in solution formation.

Samples of Zinc with only water in solution (**Figure 5.11**(b),(d),(e)) displayed irregular fracture surfaces which could result in unstable fracture. Especially in Zinc oxide samples (**Figure 5.11** (d),(e)) numerous gaps and pores were visible. Coating layer particles were uneven and spread over the surface in a random manner.

Molasses and paraffin oil improved the overall uniformity and adhesion between zinc and urea for both Zinc sulphate and Zinc oxide samples (**Figure 5.11** (c),(f))

Gelatin made a very compact and uniform membrane layer over the surface of urea and played a positive role by closely packed structure due to its film formation properties (**Figure 5.11** (h)). When gelatin was combined with Zinc oxide, a very uniform and homogenously spread coating layer of zinc particles was formed over the surface (**Figure 5.11** (g))

For Zinc sulphate, agglomerates formation and lumpy coating layer was formed (**Figure 5.11** (b), (c)) whereas the coating layer for Zinc oxide was composed of fine particles (**Figure 5.11** (d), (e), (f), (g)). Sonication of Zinc oxide and water solution had no significant advantages overall apart from uniformity of coating layer to some extent (**Figure 5.11** (e)).

5.5 Fourier Transform Infrared (FTIR) Spectroscopy

The interaction of urea and coating materials was analyzed. Different functional groups were present with IR spectra of the coated samples and uncoated urea almost exactly similar as shown in **Figure 5.12**

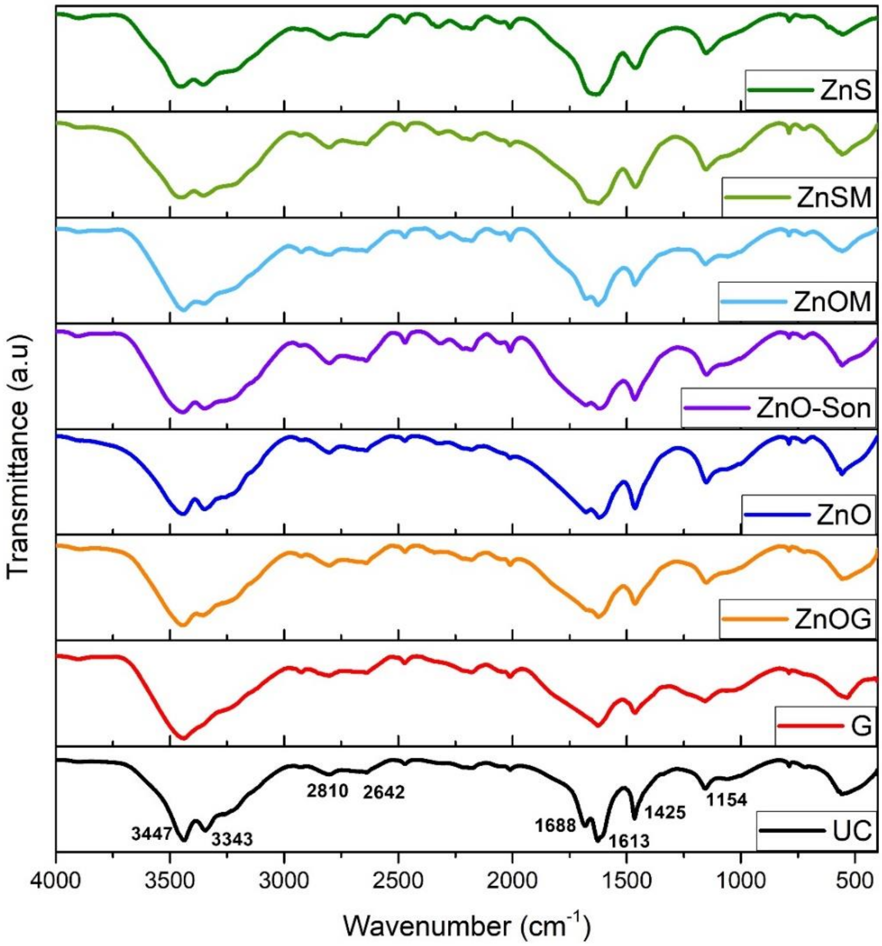


Figure 5.12: FTIR images of fertilizer samples

Corresponding peaks shown in the images could be attributed as: 3447 cm^{-1} and 3343 cm^{-1} to asymmetric and symmetric stretching vibrations of N-H, 1688 cm^{-1} to carbonyl functional group (C=O) and at 1613 cm^{-1} to binding vibration of N-H and stretching vibration of C-H. The medium intensity bands present at 1425 cm^{-1} and 1154 cm^{-1} could be associated to vibrational stretching of bonds of C-N and C-C respectively [37] [38] [39]. All the spectra and peaks of coated samples were very much alike to the spectra of uncoated samples and there were very minute changes. On the basis of similarity and no significant variation before and after modification, it can be stated that nature of bonding is not chemical and the coating materials are attached to the urea through physical bonds i.e. hydrogen bond, van der waal forces and electrostatic attraction forces.

5.6 X-ray Diffraction

XRD is significantly important technique to confirm the presence of base components in hybrid or coated materials and to study the crystallinity of the materials. The XRD of coated samples after modification showed no shift in position of peaks as shown in **Figure 5.13**. The uncoated urea sample had prominent and dominant peaks at $2\theta=22^{o}$, $2\theta=24.5^{o}$, $2\theta=29.5^{o}$ and $2\theta=36^{o}$.

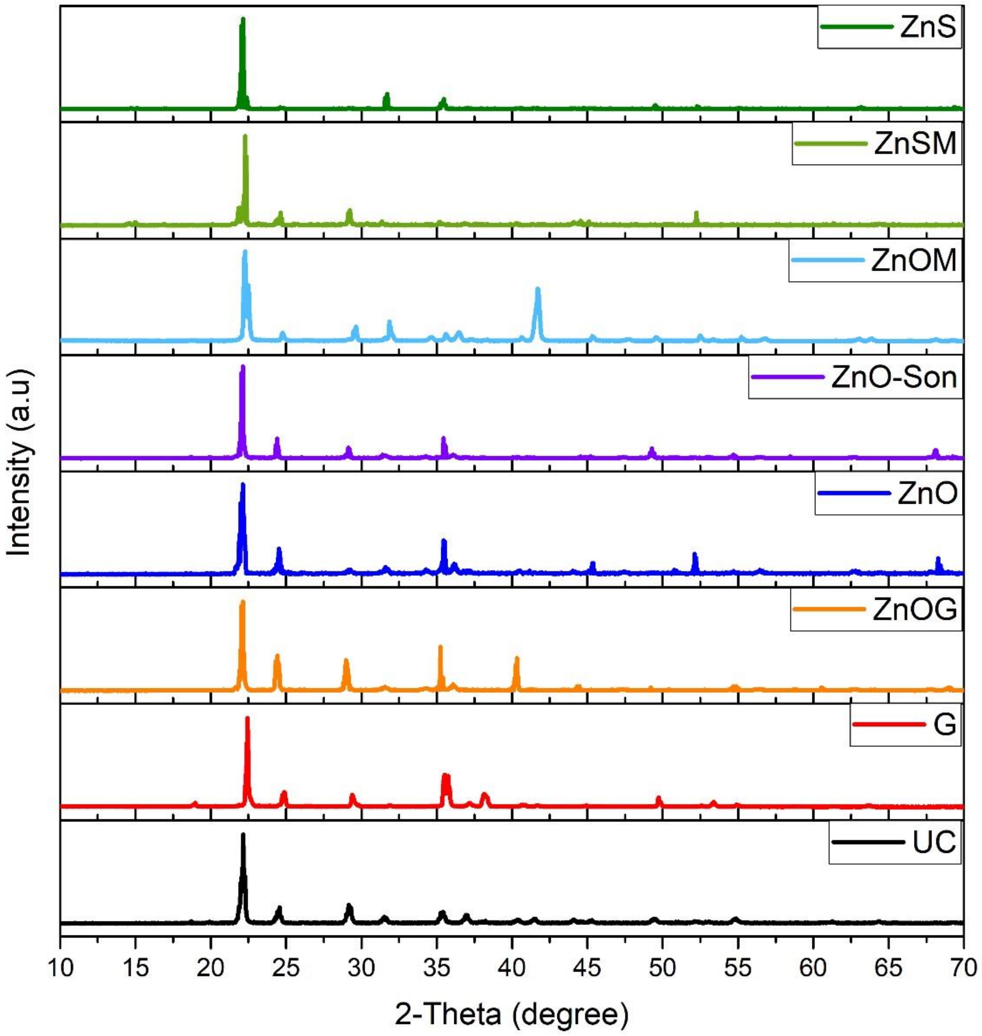


Figure 5.13: XRD images of fertilizer samples

The spectra of all coated samples showed sharp peaks similar to un coated urea. The sharp peaks shows the high crystallinity and means that clear coating has been formed on urea. The XRD pattern indicate presence of Zn in the form of Zinc oxide with prominent peaks at $2\theta=36^{o}$, $2\theta=42^{o}$ and minor peaks around $2\theta=55^{o}$, $2\theta=68^{o}$ for Zinc oxide coated samples (**Figure 5.13**: ZnO, ZnO-Son, ZnOM, ZnOG). XRD is used to analyze crystalline materials which could be the possible explanation for no new peaks in spectra for Zinc sulphate and Gelatin coated samples. It could be stated that Zinc sulphate and Gelatin were present in rather poor crystalline forms and were not detected by XRD. All of the coated samples showed sharp peaks indicating high crystallinity and means that clear coating has been formed. The spectra for all samples were almost similar and all the peaks observed could be either attributed to the base material or to component material of the coating. It can be concluded that interaction of urea and coating materials is of physical nature and the structure overall is not modified substantially [40].

5.7 Crushing Strength

Crushing strength is very important in terms that if urea gets easily fractured, the nutrients and coating materials will disintegrate and convert into fines and lost during shipping and storage [41]. The crushing strength for all samples were measured and is shown in **Figure 5.14**.

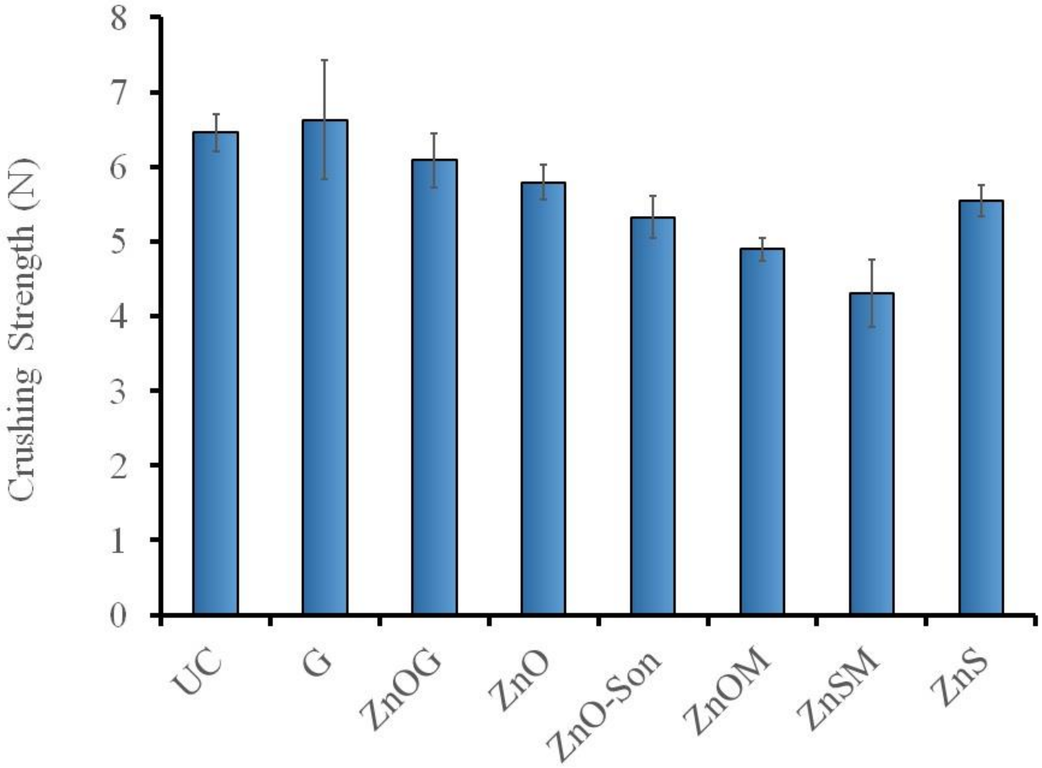


Figure 5.14: Crushing strength

Table 5.10: Crushing strength

Sample	Crushing Strength (N)
UC	6.45 ± 0.24
G	6.62 ± 0.79
ZnOG	6.08 ± 0.36
ZnO	5.79 ± 0.23
ZnO-Son	5.32 ± 0.27
ZnOM	4.89 ± 0.14

ZnSM	4.31 ± 0.45
ZnS	5.54 ± 0.21

Coating the samples did not improve the crushing strength apart from the gelatin coated urea (G) which showed only slight increase in crushing strength. Rest of the coated samples were either similar or inferior to pure urea in terms of crushing strength. Maximum crushing strength was recorded for G sample (6.62 N) closely followed by pure urea (6.45 N). The minimum crushing strength of 4.31 N was recorded for ZnSM sample. The results were satisfactory with no significant reduction in crushing strength and it can be concluded that all samples can withstand transportation and storage operations physical impacts.

Conclusions and Recommendations

Conclusions

The study was conducted to coat urea with micronutrient zinc and possibly increase its nitrogen use efficiency. Zinc sulphate and Zinc oxide were used as Zinc sources. Gelatin was applied to control urea release rate and molasses and paraffin oil were investigated as binders. All treatments were examined for their physical and chemical properties and were subjected to pot tests for their results in plants. Release rate for gelatin coated urea was also investigated. As per our study Zinc oxide was better source for providing zinc to plants and soil through coating of urea. All Zinc oxide coated samples significantly improved the Plant height, yields, N and Zn uptake and nitrogen use efficiency. Sonication of zinc oxide had no advantages and more or less similar to results. Zinc oxide alone has great potential in improving yields and overcoming zinc deficiencies. Zinc sulphate coated samples were not efficient in terms of increasing yield and nitrogen use efficiency, however it was better in terms of zinc uptake than un coated urea. Gelatin alone significantly affected the nitrogen use efficiency and yield and can be a potential fertilizer where zinc deficiencies are not severe. When used in combination with Zinc oxide, it was the best sample by improving plant height by 11 cm, Fresh matter yield by 87.8% (almost doubled), dry matter yield by 94.3% (doubled) and ANR% of pure urea from 23% to 48%. It was also the best sample in terms of providing zinc to plant and soil with zinc uptake 5 times higher than uncoated urea and apparent zinc recovery standing at significantly high percentage of 67. Zinc performed two roles for us by acting as a micro nutrient for plant and as a urease inhibitor. While gelatin controlled the release of nutrients by forming a film. Combined roles of gelatin and zinc lead to controlled release, high uptake of macro-nutrient N, reduced losses and supplication of micro-nutrient Zn to soil and plants efficiently. As per results of XRD and FTIR for all the samples, coating materials did not alter the urea chemically and were associated through physical bonds. From the manufacturing perspective, all coated samples were easy to produce requiring no alterations in existing urea manufacturing process apart from the post manufacturing coating process. None of the sample required organic solvents and all samples were completely biodegradable. Results indicate that ZnOG is a promising fertilizer which will allow farmers to provide nitrogen and zinc to plant and soil through single application. It will lead to better yields from both quantity perspective and quality i.e. nutrition perspective. All of these are important findings in contribution to environment and agriculture sustainability with urea prone to low efficiencies, hazardous losses and increasing zinc deficiencies.

Recommendations

The study could be extended and carried forward with following future recommendations:

- Pot tests can be carried out on other crops i.e. maize
- Pot tests can be carried out using half of fertilizer quantity or 75% of quantity and analysis can be carried out how much savings can be achieved.
- Field tests can be carried out with similar combinations
- Percentage of Zinc and gelatin can be optimized using different ratios.
- Release Kinetics and effect of different parameters i.e. temperatures, ph of soil can be studied through Sand column release tests.
- Nano particles can be used instead of bulk and comparison can be made.
- Zinc can be used in combination with other binders and slow release materials i.e. Starch, chitosan, Arabic gum, pectin, cashew gum etc.

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