SYNTHESIS AND CHARACTERIZATION OF ZINC-COATED UREA FERTILIZER

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Synthesis and characterization of Zinc-Coated Urea Fertilizer

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Thesis submission certificate

It is to certify that work in this thesis has been carried out by Hafiz Ghulam Mustafa and completed under my supervision in department of chemical engineering, university of engineering and technology, Lahore

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Dedication

Dedicated to my Parents, Family & Teachers

Acknowledgement

All praise and glory be to **ALMIGHTY ALLAH** the ultimate creator of this universe: from particle to stars, who blessed us with the ability to think and an eager to explore this whole universe. Countless salutations upon the **HOLY PROPHET HAZARAT MUHAMMAD (S.A.W)**: the source of knowledge and blessings for entire mankind. I am thankful to **ALLAH ALMIGHTY** who has provided my health and energies to pursue and fulfill my highest academic achievement. I am thankful to the UET that provided me opportunity to achieve my objectives.

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Abstract

Fertilizers are a back bone to any country's agricultural well-being and growth. The conventional fertilizer technology resulted in increased environmental pollution and nutrient loss. In this research premieres Control Release Fertilizer Technology (CRF) has been synthesis by inorganic salt coating on urea fertilizer for efficient consumption of urea in plant root zone and good achievements in food grain and enriched nutrients production by the plants. The synthesized fertilizer were characterized by XRD, FTIR and TGA. XRD revealed that the confirmation of presence of zinc sulphate on the surface of urea beads through their comparison with JCPDS Cards defined in data bank of XRD. FTIR analysis predicted the presence of zinc sulphate on urea beads through the detection of functional groups of product. TGA study determined the weight loss of sample with temperature and one percent retained mass indicated that the mineral zinc required high temperature for volatilization. The controlled release test also a confirmation for the presence of zinc sulphate on the surface of urea beads in which delayed time dissolution of coated urea in comparison of conventional urea were observed which emphasized on the scope of emerging technology of Control Release Coated Urea Fertilizer Technology

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CHAPTER # 01

INTRODUCTION

1.1 Introduction

Fertilizer is a crucial key constituent for achieving autonomy in food grain production and agriculture growth. Over a period of time, fertilizer consumption step-up due to green revolution and adoption of modern technology in agriculture area [1]. The main function of fertilizer is to provide the necessary bioactive molecules and ions to the soil that plays the role in efficient growth of plants. There is a functional relatedness among fertilizers, nutrients and soil that is necessary to maintain at required level [2]. The most important fertilizer among the conventional fertilizer is urea fertilizer which is widely used in agriculture setup of agriculture based country. The Uncoated urea fertilizer showed that there is an excess nutrient availability to the plants, due to sluggish usage of nutrient by plants its depicted that nutrients leaches out into the ground resources and volatilized to the environment which is the loss of fertilizer [3].

1.2 Leaching

Dissolved nutrients downward movement from the plants roots zoon with flowing water from the permeable layers of soil to the underground resources is called leaching. Leached nutrients conduce the contaminations of underground resources, particularly water. Nitrates leaching is also a major source of soil acidification

1.3 Volatilization

Movement of excess available nutrients to the environment due to their regain of gaseous state in plants root zoon is termed as volatilization. Nitrogenous fertilizer, when dissolved into water it convert into ammonium ion and nitrates ions, both ion oxides and reduces to nitrogen oxides and ammonia gas which are volatilized to environment and cause air pollution.

The main associated problems of conventional urea fertilizer has been described below, in the drawing of consumption mechanism of nitrogenous fertilizer.

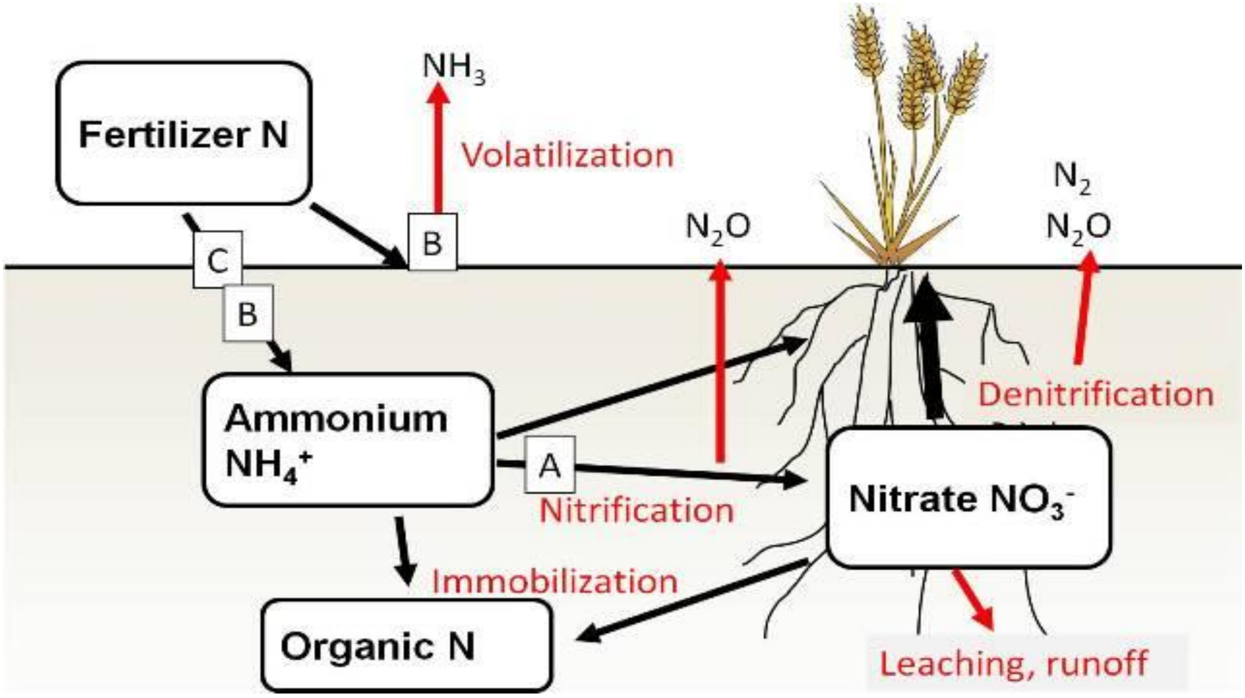

Figure 1 Fertilizer dissolution mechanism

The possible alternative to decrease nutrient loses and pollution control is to produce slow release and control release fertilizer. Recently control release fertilizer technology has been egressed as a multidisciplinary research frontier. The coated fertilizer are produced by applying the different organics and inorganics materials to the surface of conventional fertilizer to produce slow release or control release fertilizer. The control release fertilizer (CRF) has been designed to control the available concentration of biological species to the plants root zoon, leaching loss and environmental pollution [4-8].

1.4 Coating treatment gets together

- Control dust emission
- Minimize caking
- Enhance flow ability
- Stabilization of surface
- Compatibility for termination
- To create more attractive appearance
- Nutrient release modification

The number coating techniques has been originated and applied to conventional fertilizer for controlling of nutrients release in the plants root zone and minimizing the associated problems.

The techniques with their merits and demerits has been tabulated in the table given below.

Table 1 Different coating techniques with their pros and cons

Type of Coating	**Pros and Cons**
Particulates, minerals and salts coatings	Good for flow ability, anti-caking less waste of fertilizers and more advantageous for the supply of dual nutrients in single products
Water dissolve liquid coating	Particularly applied in solubility dependent fields
Polymer based coating systems	Expensive and complex processing

Minerals and salts coating is a more prominent and dual beneficial coating of conventional fertilizers.

Different nutrients salt is available as coating materials for conventional fertilizer. This is first type of coating as mentioned in above table having maximum advantages. Zn is an important constituent among the 17 essential elements that are required for the normal growth of plants. Eight micronutrients are essential for plants growth [7], Zn is one of them that plays a key role in plants with enzyme proteins involved in carbohydrates metabolism, protein synthesis, pollen formation, maintenance of biological membranes, gene expression auxin, protection against photo-oxidative damage and heat stresses, also the resistance to infection by particular pathogens . Urea coated with zinc not only enhance the return of crops, but also the amount of cereal [8] .

CRF is prepared by the coating of micronutrient zinc salt to the macronutrients urea fertilizer [9]. The current research cater a treatment for coating of micronutrient compounds on the surface of urea prills which obviate the inherent disfavors of conventional urea fertilizer. Present research will focus the multiple advantages of coating materials such as the control release of nutrients, reduces the above mentioned impuissance, the product is readily soluble in water and grant the macro and micro nutrients at the same time to the crops within single product [10].

1.5 Problem Statement

Fertilizers are a back bone to any country's agricultural well-being and growth. Fertilizers are considered crucial to meet up the nutrient demands of present day soils. The conventional fertilizer technology resulted in increased environmental pollution along with the wastage of money because of the imbalance between the concentration of the nutrients being absorbed by the plants and that being applied as an uncoated fertilizer releasing in an uncontrolled manner. This era premieres Control Release Fertilizer Technology (CRF) as a widely focused research paradigm. CRF makes use of coating treatment of solid fertilizers in-order to enrich their flow abilities, better absorption to soil, controlled dust emissions and improvised nutrient availability.

1.6 Research Objectives

To address the challenges associated with conventional fertilizer. The overall research objective is to synthesize zinc coated urea fertilizer experimentally, characterize it and to check the coated fertilizer dissolution rate in the water.

The following objectives are considered

- To study the reason of nutrients loss.
- To synthesize zinc coated urea by mineral and salt coating.
- To study coated urea and conventional urea release.

1.7 Synthesis of coated urea fertilizer

Zinc coated urea fertilizer has been synthesized through zinc salt hydrated and urea beads using physiochemical technique. The hydrated salt water molecules has been replaced by urea molecules by hydrogen bonding between partial positively charged hydrogen in urea and partial negatively charged oxygen in zinc sulphate. The complete physiochemical process has been shown here.

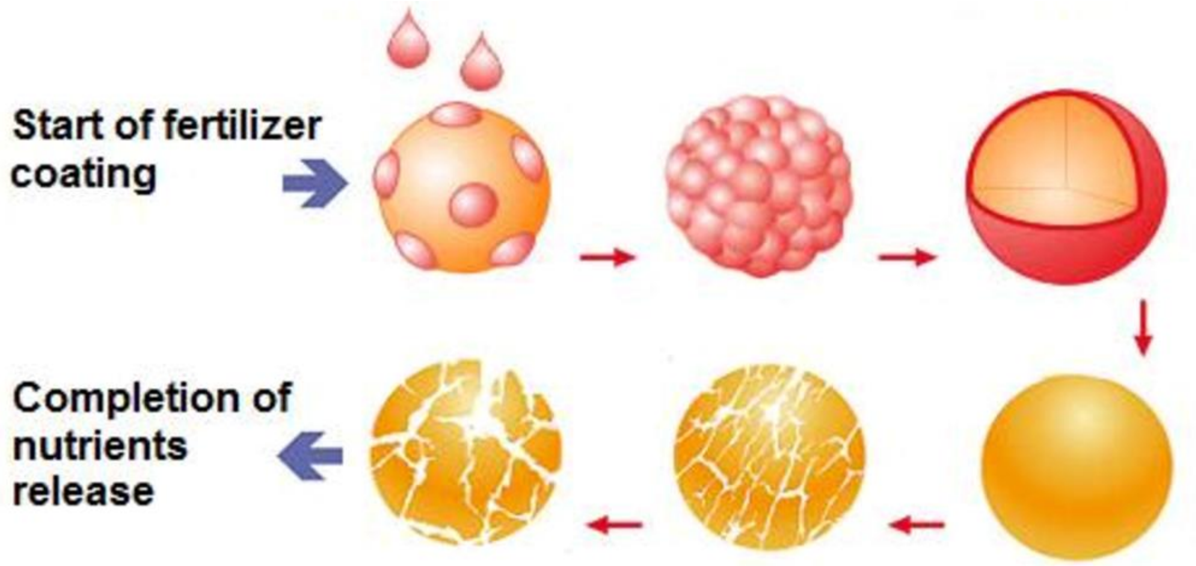

Figure 2 Coated urea Granule dissolution

1.8 The scope of study

The research mainly focused on the study of coated fertilizer. The work was to synthesized controlled released zinc coated urea fertilizer. The lab prepared coated fertilizer has been characterized by X-Rays Diffraction (XRD), Thermogravimetric analysis (TGA) and Fourier Transform Infrared Radiation (FTIR). To investigate and compare the performance of conventional fertilizer and lab prepared coated fertilizer.

CHAPTER # 02

LITERATURE REVIEW

2.1 Literature Review

This chapter reviews the synthesis and characterization of coated urea fertilizer for advancements in agriculture areas of the country as well as worldwide. A details literature review is presented for coated fertilizer preparation and practical impact on the agricultural fields.

2.2 Zinc coated urea Fertilizer

Zinc coated urea fertilizer is a product of conventional urea fertilizer and zinc sulphate. The coated urea can be produce by different physiochemical methods but the product specification varies with technique. The most appropriate technique has been applied in which the chemical bonding of zinc sulphate, the micronutrient with urea prill was achieved by applying superficial layers of exquisitely divided hydrated zinc sulphate on to the urea beads. The water of hydration displaced from the hydrated salt by urea molecule. The samples were rotated in the lab scale ball mill for the assistance of hydration reaction that ingested zinc salt on urea surface.

Wide contents of research has been carried out in past decades to find the most efficient coated fertilizer. Coating of fertilizer through diverse techniques has been carried out in different research works. The detail study of synthesis of coated fertilizer has been given below that describes previously conducted research works in different years for the different improvements in supplying of conventional fertilizer.

International Plant Nutrition institute (IPNI) USA describes deficiencies in plants that can be improve through different means such as supplying required nutrients to plants which ultimately balance their growth rate [11]. Beth Guertal et al reported that the improved fertilizers are crucial to serve feed the world's growing population, security and protection of the environment [12]. A. Shaviv, 2001; the advances in controlled release fertilizer [13]. C. Henrist ; the urea hydrolysis for the evaluation of morphology of nanoplatelets [14]. J.W. Spears; effect of different zinc sources on ruminal volatile fatty acid proportions [15]. V. D. Fageria ; interaction of crops and nutrients that can balanced through fertilizer [16]. Mojca Fir ; reported the bonding of urea with other chemicals for the production of coated fertilizer [17]. S.M. Lu 2007 ; the analysis of pure and coated urea beads [18]. Y. S. Shivay ; zinc uptake by specific field using different coating sources of urea [19]. Lal Bahadur ; the soil application of zinc uptake on tree size, yield and quality of fruit [20]. Manish Vashishtha ; the improvement of properties of urea with the application of coating materials [21]. Rui Lan ; coated fertilizer can be produce through spray coating technique for the production of [22]. The Global Development Network (GDN) continuous reporting for sustainability in fertilizer production by improving effectiveness and efficiency. Yashbir Singh Shivay 2012; coated urea improves the productivity of basmati rice. Milene M. E 2013; polymer coating for control release of macronutrients. Soumitra Das 2013; zinc is important for crops as well as for human being. IZA 201; acceleration of zinc in conventional fertilizer. N. Milani 2015; nanoparticle coating of zinc on macronutrients.

2.3 Methods for the preparation of Zinc Coated Urea Fertilizer

Many researcher prepared coated urea fertilizer by sol gel hydrolysis, polymer coating, immersion and spray coating has employed in different research works.

2.3.1 Sol gel hydrolysis

It is a prerequisite method for the preparation of coating good quality fertilizer. Corrosion inhibition totally depends upon the proper balance between number of attaching groups on the surface of urea beads and concentration of urea molecule in urea beads. Both the physiochemical reactants influence the adhesion and the density of protective coating [5].

2.3.2 Polymer coating

Different polymeric materials such as Polytetramethylene glycol, Polyurethane, polyacrylic acid has been applied with a particular binding materials for the preparation of coated urea feriltzier which only provides single effect that is control release of conventional fertilizer production in the plant root zone[5].

2.3.3 Immersion technology

Urea grannules can me immerse into the solution of coating mterials under continuous stirring , filtering, and wetting arrangements. This technique may be use for polymeric coating or may be for inorganic salts binding[6].

2.3.4 Spray coating

Coating materials' solution can be used as a spraying solution through manual pulverizer. The ouput flow of manaul pulverizer required to maintaine at required values. The agglomeration of beads can be avoid through continuous stirring of beads in a rotating mill and wetting arrangement also required at the rotating plateform of materials so that required drying of bead can done[7].

CHAPTER # 03

EXPERIMETAL TECHIQUES

3.1 Materials and Methods

3.1.1 Materials

Industrial urea (46.4%) was purchased from FFC plant, analytical grad zinc sulphate hydrated.

3.1.2 Method

The chemical bonding of zinc sulphate, the micronutrient with urea prill was achieved by applying superficial layers of exquisitely divided hydrated zinc sulphate on to the urea beads. The water of hydration displaced from the hydrated salt by urea molecule. The samples were rotated in the lab scale ball mill for the assistance of hydration reaction that ingested zinc salt on urea surface at ambient conditions for 30 minutes. The so-wetted urea prill was dried in an oven to remove extra water and to finish the product.

3.2 Experimental setup

Hydrated salt were converted into powder form for the enhancement of surface area for efficient reaction yield

Crystal zinc sulphate Powder zinc sulphate

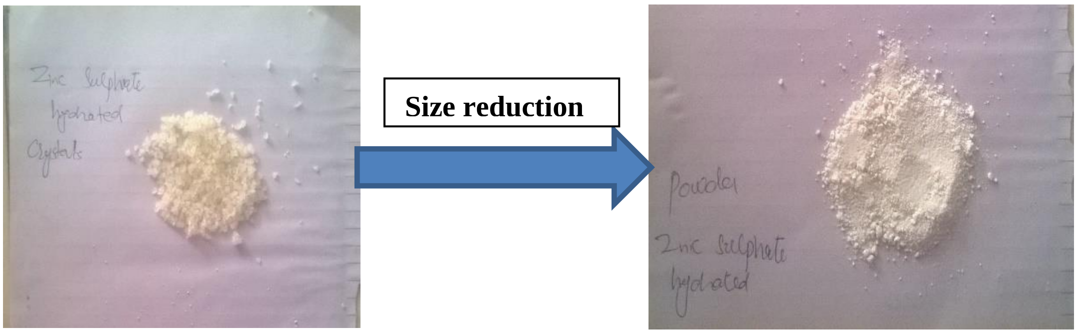

Figure 3 Raw materials preparation setup

In powder state maximum salt molecule avail reacting sites with urea molecules for efficient coated product. Powder salt and urea beads were placed into the jar mill for rotation. Mechanical rotation assist the reacting molecules to reach more and more close to urea beads surface and get reacted

Figure 4 Mechanical rotation mill

Synthesized samples need heating for extra water replaced by urea molecules, removal. Samples were placed into the oven for specified time and finished product was received.
Five different samples were prepared by varying the amount of zinc sulphate on to the urea beads. Prepared samples were analyzed through control release test and observed data was plotted and interpreted.

Figure 5 Synthesized samples

3.3 Coated Urea Characterization

Phase identification and structural study of lab prepared zinc coated urea was performed by X-rays diffraction with scan angle variation 15^{o} to 90^{o}, step size 0.4 degree and step time was 1sec. The structural parameters were calculated by standard relation**.** Presence of different function group in the samples were determined by FTIR spectra by comparing with literature values. Thermal decomposition of prepared samples were determined by TGA analysis at the temperature range (0-600) K in nitrogen environment.

CHAPTER # 04

CHARACTERIZATION TECHNIQUES

4.1 Characterization Techniques

4.1.1 X-rays Diffraction:

X-rays diffraction is a tool used to identify the phase of crystallize materials, overall spacing between layers of atoms, orientation of atoms in a grain, the size, shape of a crystal and internal stress of small crystalline region. This technique uses Scherer equation for the calculation of size of crystal through crystal structure and atomic spacing

$$D = \frac{K\lambda}{\beta cos\Theta}$$

The working principle of XRD, x-rays are generated from cathode ray tube, filtered to give monochromatic radiation and directed toward the sample. The refracted rays wavelength were related to diffraction angle

Crystal structure and phase analysis of lab prepared catalyst samples were studied by XRD pattern using Cu Kα1 at room temperature. Indexed XRD pattern of samples have been presented here below, in 2-theta range of 15^o-90^o. All the recorded XRD patterns represents the well crystalline samples and revealed the presence of zinc sulphate on the surface of urea beads. The peaks of zinc sulphate at respective 2-theta position were confirmed by JCPDS card No. 01-079-0208 and that urea was confirmed by JCPDS card number 00-9-204.

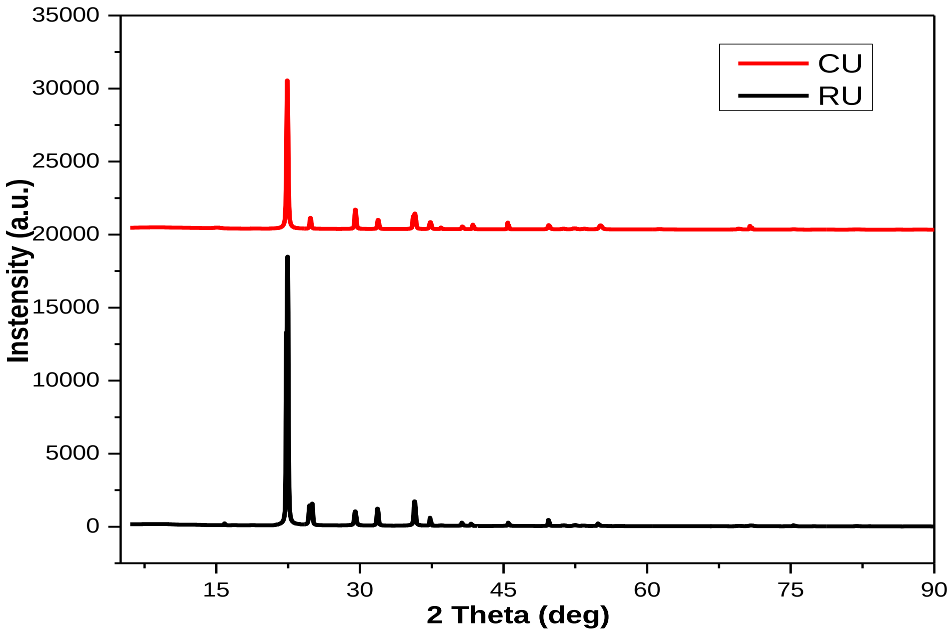

Figure: 6 XRD Analysis of Raw and Coated Urea Samples

4.1.2 Thermogravimetric Analysis

The Thermogravimetric Analyser (TGA) is an important laboratory tool used for material characterization. TGA is used as a technique to characterize materials used in chemical, food, pharmaceutical, and petrochemical applications.

Mass of a substance is monitored as a function of temperature or time in thermogravimetric analysis. A controlled temperature program in a controlled atmosphere is given to sample. In simple words, weight loss or gain of a sample specimen with increase and decrease in temperature is measured.

A TGA consist of furnace in which sample pan is placed that is supported by measuring balance. The purpose of furnace is to cool and heat the mass of the sample. The temperature is monitored during the experiment. To control the environment of sample purge gas is introduced, gas may be inert or reactive. X- Axis on TGA thermal curve is displayed as temperature or time and Y- Axis can be displayed as weight (mg) weight percent (%). A TGA thermal curve is displayed from left to right. A descending TGA thermal curve indicates a weight loss. Sample preparation depends on nature of sample. However there are some suggestions which should be considered while preparing sample mostly in TGA experiments inert sample purge gas is used. This is done so that sample decomposes with temperature. Heating a sample in an inert atmosphere is called pyrolysis. Sometime a reactive sample purge gas such as oxygen is used. This is used to identify the percent carbon in a material.

Table: 2 analysis of TGA for coated urea

Urea

T ^{0}C	%age Wt Lose
195-200	6.59
200-260	19.4
260-370	65
370-600	6.1

Zinc sulphate

T ^{0}C	%age Wt Lose
180-210	7.5
210-290	16
290-400	61
400-600	8.5

The thermogravimetric analysis of zinc coated urea fertilizer were also performed to determine the mass lose as a function of temperature. The weight lose with temperature change has been shown here.

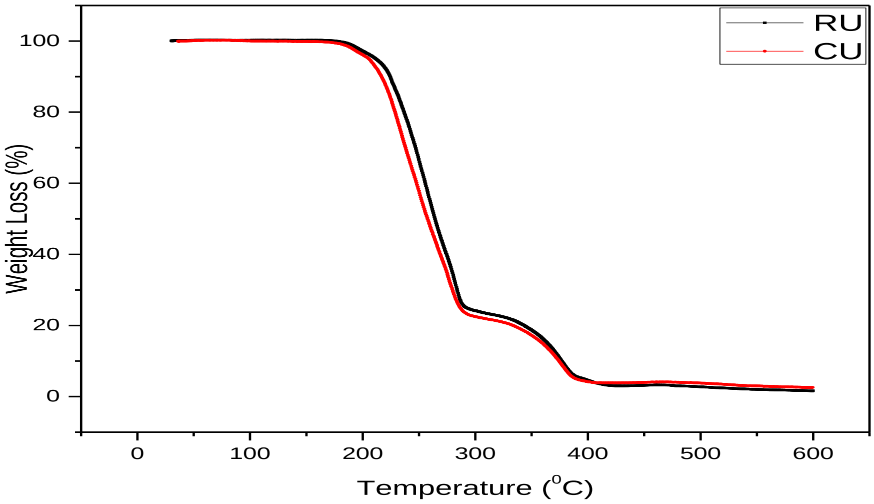

Figure: 7 Thermogravimetric Analysis of Raw and Coated Urea samples

4.1.3 Fourier Transform Infrared Radiation Analysis

Infrared spectroscopy is useful techniques for identifying pure organic and inorganics compound present is the sample. Infrared radiation is usually does not possess sufficient amount of energy to cause electronic transition, it can induce transition in the vibrational and rotational states associated with the ground electronic state of the molecule. Infrared spectroscopy is a less satisfactory technique for quantitative measures than its ultraviolet and visible region due to low sensitivity and deviation from Beer's law.

The molecular species in the samples absorb infrared radiations and produce a unique infrared spectrum that will compare with the available database of Fourier Transform Infrared Radiation software

Table: 3 FTIR analysis of samples

Sample		**1**	**2**	**3**	**4**
Component	**Frequency**	**(cm^{-1})**	**(cm^{-1})**	**(cm^{-1})**	**(cm^{-1})**
Urea	**Literature**	695-745	1040-1070	1430-1560	3450-3540
	Experiment	720	1030	1480, 1550	3490
Zinc Sulphate	**Literature**	755-945	1080-1120	1470-1540	3490-3520
	Experiment	760	1095	1450, 1520	3510

The Fourier Transform Infrared Radiation of zinc sulphate was done to check the presence of urea and zinc sulphate into the sample. Coated urea sample was ground to powder state and place at the sample analyzing place of instrument, in result the IR spectra was generated. The wave number of samples were compared with literature values of zinc sulphate and urea, it confirmed that the samples contains urea and zinc sulphate.

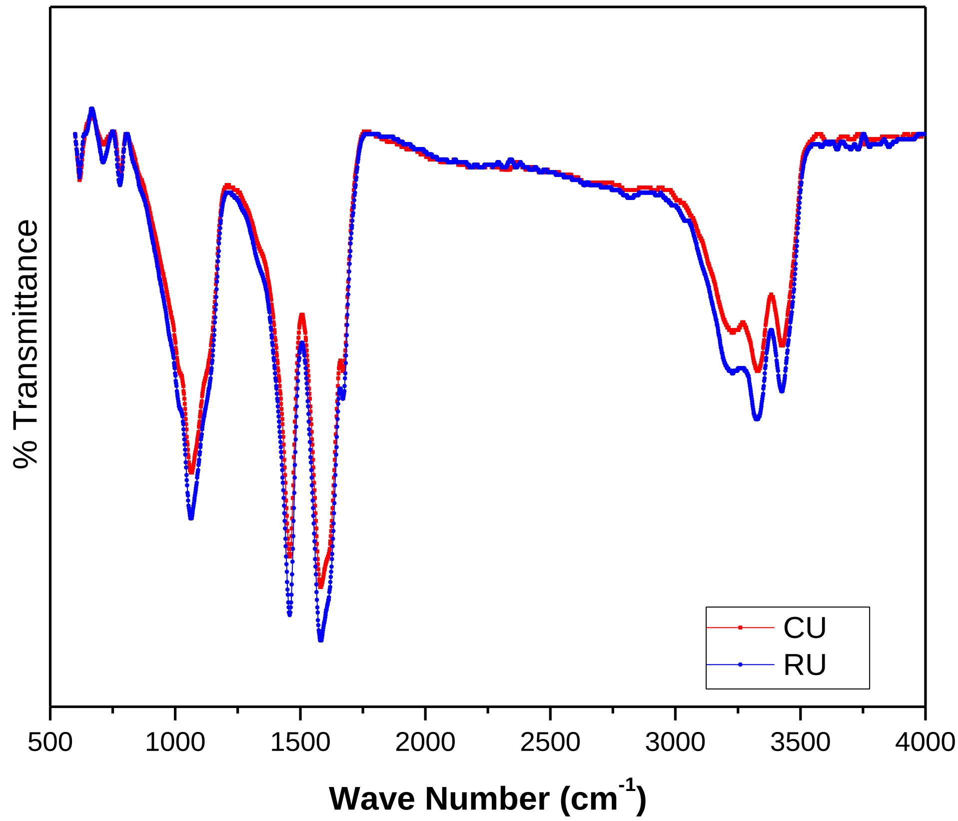

Figure: 8 FTIR Analysis of Raw and Coated urea samples

CHAPTER # 05

PRACTICAL COMPARISON BETWEEN RAW UREA AND COATED UREA

5.1 Control release rate test

The raw urea (RU) and coated urea (CU) release rate were analyzed at ambient condition in distil water. Five different Raw Urea samples and lab prepared coated urea samples were placed into five different distill water beakers and their dissolution timings were noted. The observed data was analyzed through graph.

Figure: 9 Control release testing

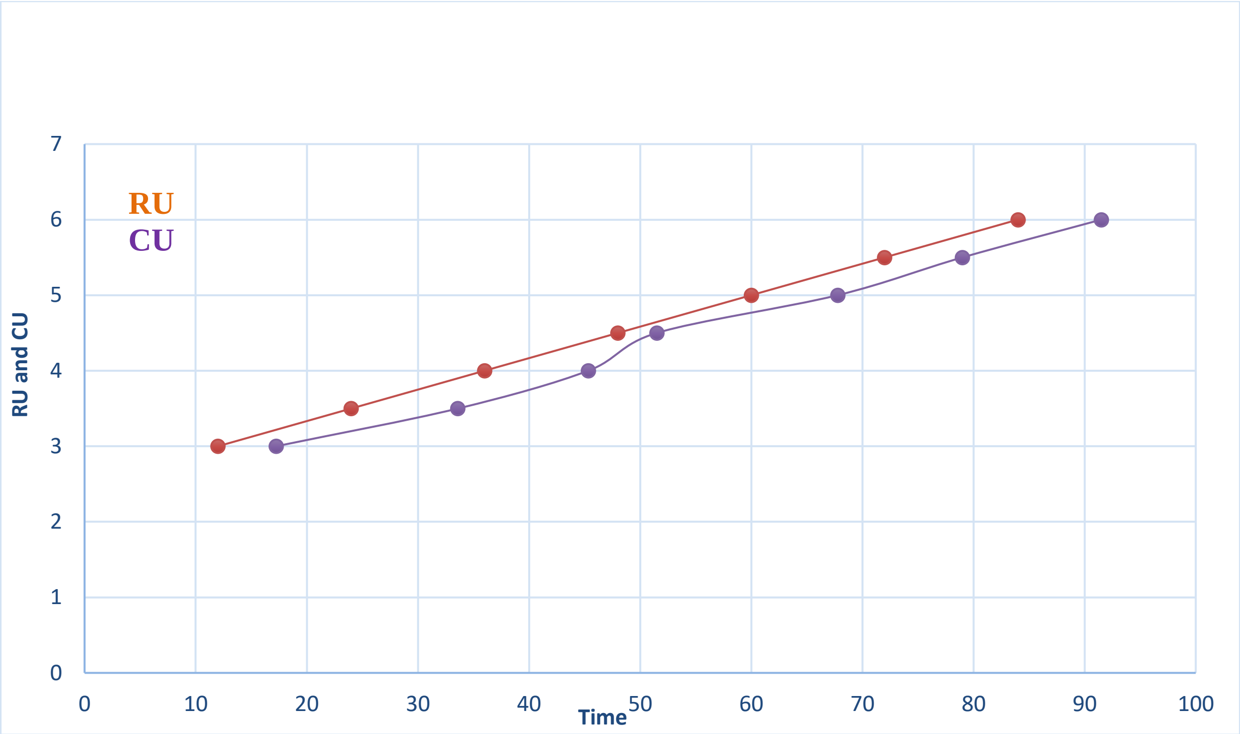

Figure: 10 Plot of Raw and Coated urea analysis

5.2 Interpretation

It is cleared from the above graph that raw urea were dissolved early than coated urea samples. Coated urea will release the nutrients in a controlled manners that will balance the absorption and availability of biologically active molecules in root zone. It this research coated material will provide control release and micronutrient availability in a single product.

The absorption of nutrients by the plants without any excess available nutrients has been achieved with coated urea delayed dissolution. Zinc sulphate Coated urea in this research also confirmed that its fulfilled micronutrients needs of plants through coating materials

5.3 Effect of nutrient zinc on plants

Zinc sulphate importantly enhance the zinc concentration in leaf tissues, fruit skin and fruit pulp. It's also increases the fruit size, weight, length, breadth, and pulp weight. Coated urea fertilizer strengthen the root tissues, plants size and greenery of live fields. The marked difference with application of conventional fertilizers and zinc coated fertilizer can be observe through visual assessment of plants growth that also present below here.

5.4 Practical Impact Visualization of Coated Urea

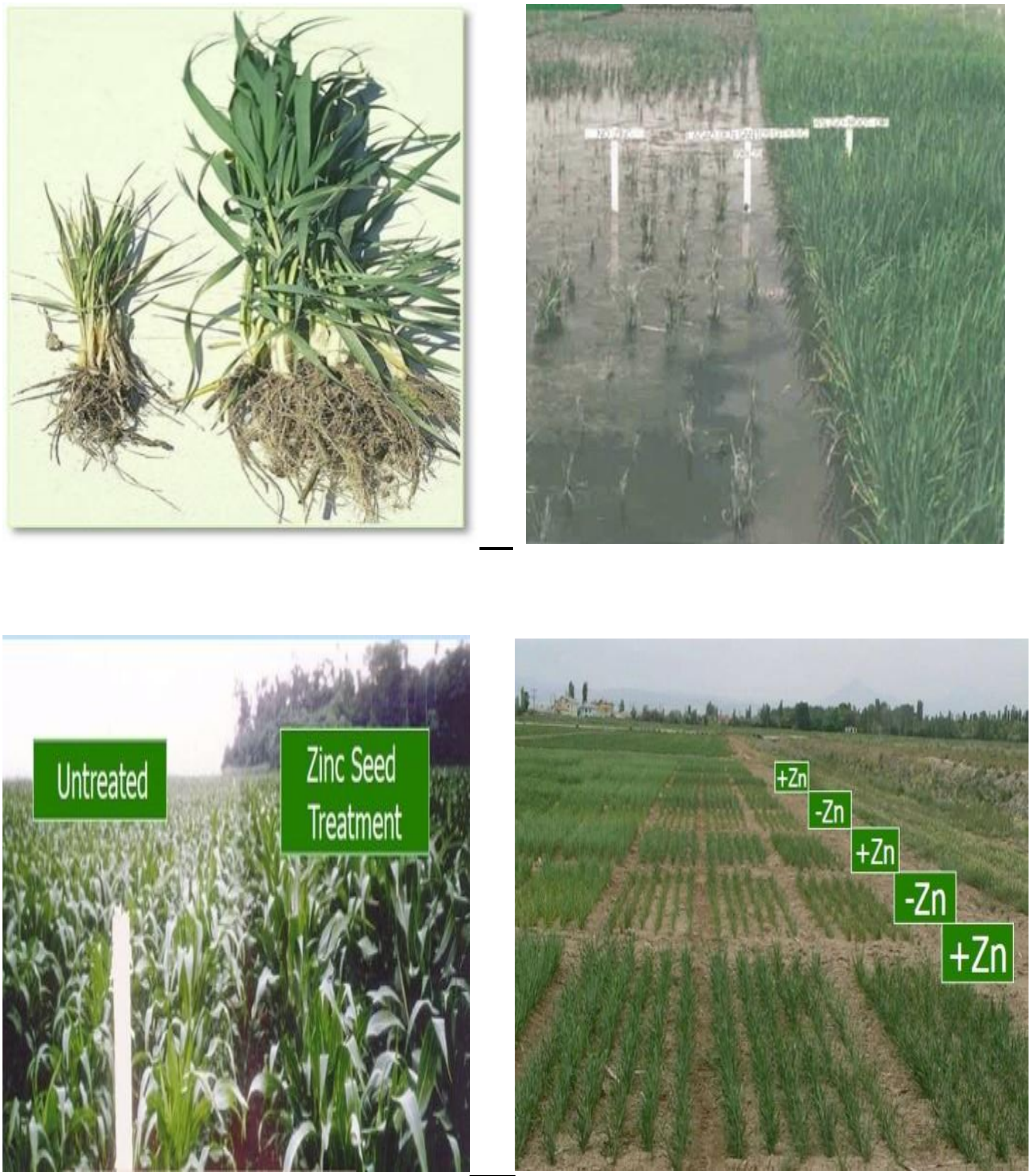

Figure: 11 Practical Visualization of Coated Urea

5.5 Conclusion and recommendations

5.5.1 Conclusion

The zinc coated urea has been synthesized by hydrated salt of zinc suphate with urea for control released nutrients to plants in their root zoon. The raw urea and coated urea were characterized by FTIR, TGA and XRD techniques. XRD analysis were confirmed that the synthesized coated urea was well crystalline in nature. The results of lab prepared coated urea showed better release rate profile than raw urea. The lab prepared coated urea very good practical greenery and riche micronutrients products by the plants

5.5.2 Recommendation

Better knowledge is necessary for the synthesis of micronutrients based coated urea fertilizer. The investigation of coated urea release rate would be test on every prepared sample are recommended, for making coated fertilizer study much more comprehensive

- Different micronutrient based chemical can be used as a coating materials for raw urea.
- The prepared models can be used for simulations, for further verification of coating materials on the surface of urea.

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