Synthesis and Characterization of Zincated Fertilizer

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Synthesis and Characterization of Zincated Fertilizer

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Dedication

This thesis is dedicated to my Imam e Hussain (A.S)

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

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Abstract

Zinc is an essential component for the healthy growth of plants and animals. Zinc concentration level in different arable soils of the world is very low. Owing to continuous crop production, the amount of Zinc is decreasing day by day in arable soils. Urea is the major macronutrient fertilizer used for the healthy growth of plants. Combining urea with zinc can give a perfect solution, to increase zinc coated fertilizer use. The focus of this research was on synthesizing and characterization of zinc coated Urea fertilizer. Zinc Oxide particles were coated on Urea granules by different techniques i.e. wet coating and slurry coating. Different binders were being used for coating purpose. The coated urea granules were investigated through different analytical techniques like SEM, XRD and XRF to know the morphology, structure of coating and composition respectively. In both coating techniques, Slurry coating technique was best because in this technique all coated particles of zinc oxide were of uniform size and coating efficiency was very high as compare to wet coating technique. In wet coating, coated zinc oxide particles were of not same size, large lumps and irregularities were seen on the surface of granules in SEM images, amount of zinc coated was low. In all the binders, Slurry used in Zinc Coated Urea 7 containing molasses, paraffin oil and water mixed with zinc oxide was the best of all. By using this binder slurry, the coating efficiency of zinc was very high. The release rate of zinc from all coated granules was measured up to 24 hours. Among all, release rate of zinc in Zinc Coated Urea 7 (ZnU7) was the steadiest, while using other binders or slurries zinc release rate was either so fast or so slow. The amount of dust produced in zinc coated urea 7 was comparatively lowest of all samples. Over all, it was observed that coating of zinc oxide by slurry containing molasses, paraffin oil and water was the best in term of coating efficiency, uniformity in size of coating particles of zinc oxide, morphology and release rate of zinc oxide.

Roman	**Nomencalture**
K	Dissolution rate constant
K_{sp}	Solubility Constant
r	Rate of dissolution

Abbreviations

Zn U1	Zincated Urea 1
Zn U2	Zincated Urea 2
Zn U3	Zincated Urea 3
Zn U4	Zincated Urea 4
Zn U5	Zincated Urea 5
Zn U6	Zincated Urea 6
Zn U7	Zincated Urea 7
Zn U8	Zincated Urea 8
HBW	Honey Bee Wax
GA	Gum Arabica

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Chapter 1

Introduction

Global population is increasing exponentially; as the population is increasing the demand of food is also increasing[1]. To satisfy the demand of food and fiber, the agricultural sector is using huge quantity of fertilizer, which in turn increases the cost of food production[2].For plant growth fertilizers are quite necessary to provide both macro and micronutrients nutrients in different proportions[3]. It is investigated that 30–50% of cropyields in various regions of the world are just because of fertilizers. Globally, the use of fertilizers for better cropyield has increased dramatically in last 64 years[4]. In 2006, as claimed by World Resources Institute that, two-thirds of all fertilizer are being consumed by just five countries, viz., United States, Brazil Indonesia, China and India; China is the biggest user of fertilizer around the globe, it consumes 55925.6 thousand metric tons, which is 32.9% of the total world[5]. In India, fertilizer application has risen so high to 132 kg ha^{-1} in 2011 from 1 kg ha^{-1} in 1952[6].

Among different micronutrients incorporated in fertilizers, Zinc is very essential for the sustained growth of Human beings, crops and animals because of its nutritional demand. Zinc deficiency occurs globally, especially in tropical and temperate zones [7, 8].Owing to zinc deficiency the agricultural productivity and human health, both are being affected[9] .Globally of all arable soils of the world, 49% are Zinc deficient[4, 10-12]. Zinc deficiency occurs in almost every zone but deficiency varies from region to region [13-15]. In some regions Zinc deficiency is low and in some it is very high. Zinc deficiency in crops is a global micronutrient problem and may be responsible for reductions in yield up to 40% without showing symptoms of any disease[16]. The Food and Agriculture Organization (FAO) has studied the deficiency of zinc in arable soils. In one out of every two cases was zinc deficient[4]. If we analyze the different part of plant, we can easily asses the amount of zinc in crops and in soils where plants are grown.

In zones, Where the yield of crops is very low without other proper cause like disease or drought[17, 18]. Farmers must try to check the amount of zinc in their soil. There is high possibility that soil would be zinc deficient [19]. Symptoms of zinc deficiency like chlorosis, stunting, rosetting and little leaf can be easily investigated. Different chemical forms of zinc have been used as fertilizers to overcome the deficiency of zinc including zinc sulphate ($ZnSO_4$) in monohydrate form as well as in heptahydrate form, zinc carbonate ($ZnCO_3$), zinc nitrate Zn $(NO_3)_2$, zinc chloride ($ZnCl_2$) and zinc oxide (ZnO)[20]. These zinc based chemicals are altered to a form in which it is highly available to crops for sustained growth. These chemicals vary in zinc content, cost and effectiveness for crops on different types of soils[21]. Among all these chemicals Zinc Oxide is highly available to crops from 50% to 80% and is the most cost effective[22].

Soils where the level of available zinc is low, is mainly due to high value of PH of the soil, low moisture content and less organic content[1, 5, 11, 12]. Soils which are sandy or acidic often lack in zinc if not treated properly will reduce the amount of yield. Even in soils which are not zinc deficient, zinc fertilization is necessary to replenish the amount of zinc removed by continuous farming of crops[4].Zinc is an essential micronutrient and component of biological ecosystem. The issue of zinc deficiency receiving attention globally because of reports about Zn deficiencies in all living organism. Zinc is the only micronutrient which is highly deficient in human beings[16].

It is estimated that about one third of the world's populations is being affected because of zinc deficiency [23, 24]. About 100 million Chinese mostly living in villages are zinc deficient. It is alarmingly a very huge figure of human population who are suffering just because of zinc deficiency[20, 25, 26].Coating of granules of urea with 1.0% ZnO gives higher productivity of rice and wheat[27].Zinc oxide has been used in different applications for hundreds of years. It is reasonably considered as perfect engineering material with production approaching more than one million ton per annum [28, 29].Since last 2000 years Zinc Oxide is being used as a major part of the medicine used for the treatment of carbuncles and boils[30, 31].

1.1 Back Ground

Zinc is the most desirable micronutrient for the primary, secondary and tertiary growth of crops[32]. Crops take up zinc in its divalent form. At this level of research, it is still unclear that whether zinc moves into the plant by facilitated diffusion or there are special transporters inside the body of plants which suck the zinc and transport it towards the cells and tissues, where zinc is needed[33, 34]. Scientists have agreed that both mechanisms operate. Nearly 90% of zinc is being transported by diffusion towards the roots of plants[6]. Soil moisture plays a major role in lateral movement of zinc inside the body of plants, and this is why arid zones and semi-arid zones are frequently more zinc deficient[35].

Zinc is mostly found on the upper surface of the soil [36]. A plant will only be able to use the zinc, when it is dissolved in the soil so that it can diffuse into the roots of the plant[37]. Zinc present in the soil exist in different forms, it can be the ionic form, complex form zinc hydroxide, zinc chloride and zinc carbonate. In calcareous soil, where ph. of the soil is very high, zinc exists in its carbonate form. Zinc carbonate plant cannot take up[38]. So in carbonate form, how much zinc is available in the soil, it is of no use for plant growth. Presence of excess level of phosphorous and copper in the soil is also responsible for zinc deficiency of the soil. Copper and phosphorous both forms complexes with zinc, Which are of no use for plants[1, 14, 21, 26, 39]. On the other hand, use of magnesium can increase the availability of zinc and its uptake by plant through roots[40].

1.2 Zinc Deficiency in Plants

Symptoms which indicate the deficiency of zinc in plants include chlorosis (deficiency of chlorophyll) in new leaves of plant, stunted saplings and fully grown plants and twisted edges of leaf. Wheat, rice, onions, corn, potatoes, barley, soya bean, falx and sugar beet crops are highly affected due to deficiency of zinc[41-44]. Zinc deficiency lowers the yield of crops and profit of the farmers.Symptoms of deficiency zinc in wheat become visible after three to five weeks of emergence of saplings and in paddy rice between two to four weeks[45, 46]. In soils where zinc is highly deficient, wheat growth is poor and in this situation, if we treat seed with **trace Zinc-Manganese** or **trace Zinc** particlescan enhance the seed germination and seedling growth[38, 47-50].

1.3 Metabolic roles of Zinc in Plants

In metabolism of plant, Zn plays a lead role in all biochemical reactions which occur in plants. Zinc has greater effect on synthesizing of long polyamide chains and amino acids.Crops like maize and sugarcane due to zinc deficiency have reduced growth rate and slow metabolism [31, 40, 48]. Zinc controls the conversion of carbon dioxide into different biochemical structures. Zinc is a one of the essential component of enzymes such as catalase and superoxide dismutase[8].Zinc helps plant to produce auxin, growth hormones, chlorophyll, carbohydrates and starch. So, total metabolic system of plant can be easily disrupted just because of zinc deficiency. Growth of plant can never be good without zinc [31].

1.4 Zinc Deficiency in Human Beings

The deficiency of zinc with vitamin A is being considered as the biggest problem of the world stated by the group of eight economist including five Nobel laureates at Copenhagen consensus (www.copenhagenconsensus.com). They concluded that if world major powers not focus on this problem. The developing and under developing countries will face big challenge of health crisis [5, 6, 41, 50]. In 2002, according to report of WHO zinc deficiency was the 5th major factor responsible for illness in economically poor countries. Almost half of the population of the world is being affected due to deficiency of iron and zinc [27, 29, 39].

Zinc performs lot of duties in human biochemical system including protection of integrity of biological hormones, synthesis of polypeptide chains, maintains the genetic code of DNA .It is major component to maintain the immune system of human beings[2, 4, 26, 32]. It protects us form dangerous infectious diseases, helps human to face psychological stress. Diarrhea and other infectious disease like pneumonia are normally found in poor countries due to deficiency of zinc [2, 25].Newborns infants mental development is highly affected due to deficiency of zinc.450,000 kids die every year due to deficiency of zinc which is 4.4 % of total kids death rate every year in the globe[2, 4, 20, 22, 25, 27, 51].

Zinc deficiency is wide spread across whole the South Asia. Mothers are highly affected in subcontinent during pregnancy, due to deficiency of zinc many maternal diseases transfer to kids during delivery of baby [26, 30, 31, 52, 53]. A survey conducted in Indian state of Haryana to know the exact figure of women who are zinc deficient. Result was quite shocking 65% of pregnant women were zinc deficient. The figures showed that 86 % of them were taking less amount zinc compare to recommend 15 mg per day [26, 30, 31, 47, 52-57].Owing to poor dietary intake in subcontinent; almost 25% Indians are zinc deficient [53, 58, 59].

The data indicate that, which we got from different resources, there must be sufficient level of zinc in the soil [47, 53, 55-59]. So that nutritional deficiency due to zinc should be overcome. Seeds which have sufficient amount of zinc in early growth have most positive effect[60].

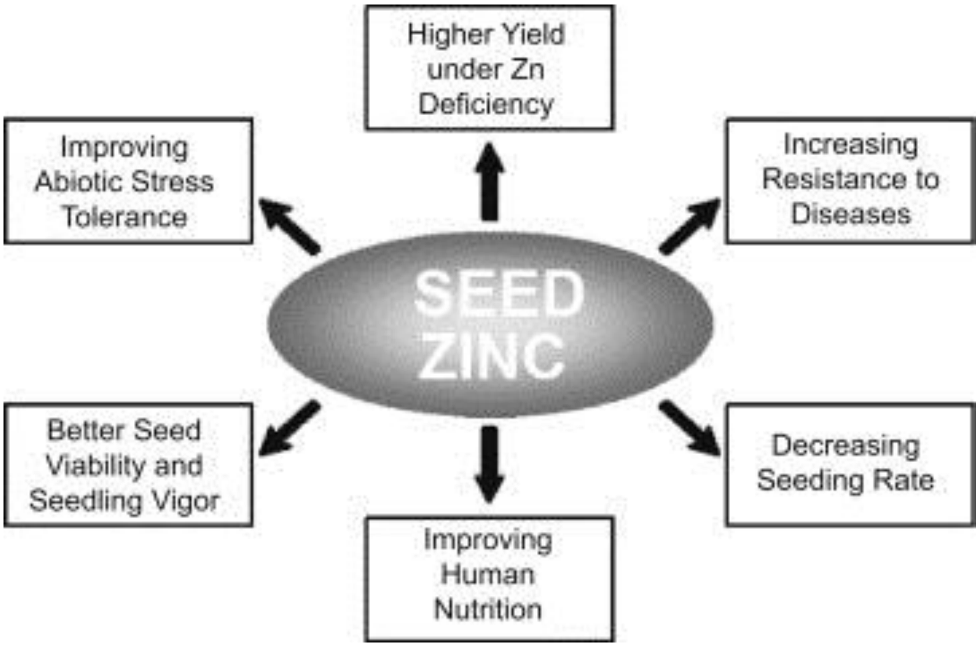

Figure 1 Effect of Zinc Deficiency on Living System

For this purpose, zinc must be applied to the soil with fertilizer. It will not only enhance the grain concentration but also the health of human beings[9].

Chapter 2

Literature Review

Malnutrition due to lack of nutrients, both macro and micro is a top priority problem in under developed countries. Currently zinc deficiency is being considered as the hot issue because of health crisis in third world countries. Women and children are highly affected due to deficiency of zinc. People are unable to take the recommended amount of zinc[61]. Dietary intake which we take in the form of staple food is also zinc deficient. Major crops which are used as staple food such as wheat and rice contains less amount of zinc as compare to the demand of body. When plants don't get proper amount of nutrients, how can they provide us the proper supplement of nutrients[62].

Zinc deficiency issue along with the deficiency of vitamin A has been raised in different international conferences[48]. Many researchers have evaluated it as next eminent threat to humanity in terms of health if not properly treated by international community. Zinc deficiency is normally found in the human beings of those regions where zinc is low in soil. So, it is quite simple to understand that if plants or crops of that region are not getting proper amount of micronutrient (zinc) during their growth[63]. There will be less zinc in grains and fruits. So the fruits and grains of that zinc deficient zones provide less amount of zinc to human beings. Human population of that zone also suffers[51].

South Asia is also in those zones of the world which are zinc deficient. Wheat and rice is staple food of subcontinent[40]. Owing to continuous cultivation of wheat and rice, the soils of subcontinent are zinc deficient. Nearly 50 % of subcontinent's soil is zinc deficient [37, 64, 65].48,000 children die each year in India just because of zinc deficiency. In Pakistan mothers of rural areas (villages) suffer from different diseases due to poor immune system and deficiency of zinc. Cereal grains also contain high amount of antinutritive compounds which plays havocs on the health of children and pregnant woman. Presence of antinutritive compound like phytates with the deficiency of zinc, adds the amount trouble for the health of newborn babies and pregnant women[66].

Compared to pulses, fruits and other dietary intakes, staple foods have very low concentration of zinc in grains [67, 68]. The most malnourished children lives in subcontinent.61 million children under the age of 5 in India have very poor and stunted growth. Globally all the children globally which have stunted growth are mostly due to deficiency of zinc and 34% of them lives in India [33, 34, 67, 68]. Zinc deficiency causes not only the stunted growth of human beings but also of plants[69, 70]. In south Asia, Zinc micronutrient deficiency is the biggest problem in arable soils, particularly for the crops which are the source of staple food like wheat and rice. It is intensely needed to bio fortify the crops so that we could get enough amount of zinc in grains. Zinc will not only increase the amount of grain concentration but will also raise the standard of health of human community[58].

Zinc deficiency in Pakistan is because of acidic nature of soil, high PH, low organic and continuous cultivation of crops on soils. So to compensate the loss of zinc, it must be applied to the soil for better growth of crops. Otherwise stunted growth and different diseases will occur in plants [23].It will have bad impact on the economy of country and poor farmers will suffer a lot. Micronutrients are applied individually as well as with the macronutrient fertilizer. Normally micronutrients are being coated on the surface of the macronutrients. In this way not only micronutrient is being supplied to the soil but also release rate of urea can also be controlled [18, 19, 71].

The mobility of zinc in the soil is very limited due to macro nutrients which are in high amount and soil particle; it forms sediments and clusters with the soil particles[14-16]. So its solubility and mobility in the soil is very limited. If the mobility of zinc in the soil is very high, there will be very high solubility and fertilization of soil will also be very high. In 1991, DG Westfall and his coworkers compared different zinc based fertilizer in term of effectiveness with zinc sulphate[1, 14-17, 72].He concluded that if these zinc based fertilizers like are in powder form ,they will be as effective as zincsulphate solution in low pH acidic soil[1, 17-19, 71].

In 2014 McLaughlin investigated that ZnO and $ZnSO4$ can have almost nearly same effectiveness if properly mixed in the soil. But if it is banded the effectiveness of ZnO will also be reduced[23, 24, 51].The environment which surrounds the granule of fertilizer around, pH and the nature of the soil plays a key role in the effectiveness, solubility and availability of the zinc to the soil[27, 32, 39].It has been investigated that in properly homogenized soil, zinc solid liquid partitioning and mobility is related to pH of the soil. However environment around the fertilizer is very different in reality [4, 8, 22, 26-29, 32, 39, 52].

Solubility and mobility of zinc particles can be increased and decreased due to many reactions. Solubility can also be affected by the biological transformation, dissolution, precipitation, adsorption and desorption[4, 8, 22, 26-29, 32, 39, 52, 73, 74].Despite of very high demand of zinc and its deficiency in human and crops, zinc based fertilizers are not being used to required level in Pakistan. Zinc fertilizers like ZnSO4, ZnSO4.H2O and ZnSO4.7H_2O are not as such easily available in Pakistan[53]. If these fertilizers are available, they are too expensive for normal farmers to buy. Quality of these zinc fertilizer is also a big concern. Hygroscopic nature of zinc fertilizer also restricts it to apply on the soil. In turkey zinc coated on macronutrient fertilizer have been applied to the soil. Urea is the most used macronutrient fertilizer Pakistan [30, 31, 52].

If we enrich the urea fertilizer with the zinc it will be a best way to supply zinc to the soil in most economical way [26, 47, 53]. Researchers from *Agriculture Research Institute Tandojam, Sindh and Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad–38040, Pakistan* have published excellent work indicating that urea enriched with zinc not only increase the yield of wheat and rice but also the amount of zinc in the grains[62]. If we enrich the urea with 2% zinc, it will benefit us in two ways first it will be economically cheap and second it will enhance the yield with high concentration of zinc in the grains .Benefit to cost ratio by applying zincated fertilizer will be very good[12].The effect of urea coated with the zinc on yield of grain of rice and grain zinc concentration and its economic analysis.

Table 1 Effect of Zincated Urea on Yield of Rice and Wheat

Treatments	Zn added (kg ha^{-1})	Grain Yield (ton ha^{-1})	Zn concentration (mg kg^{-1} DW)	Benefit (USD ha^{-1})	Benefit: Cost Ratio
Uncoated Urea	--	3.87	27	--	--
0.5% Zinc Coating	1.3	4.23	29	95	96
1.0% Zinc Coating	2.6	4.39	33	152	77
2.0% Zinc Coating	5.2	4.60	39	216	55
3.0% Zinc coating	7.8	4.76	42	266	45

This data has been taken from two year trials of agricultural fields[64, 65].

Chapter 3

Aim of Project

Zinc a micronutrient most essential element for the early and proper growth of all living organisms including plants, animals and human beings. Zinc deficient plants show stunted growth and also leave impact in the form of poor yield. The amount of zinc in the fruits and grains of stunted plants is also very low. To overcome the deficiency of zinc in plants, animals and human beings, it must be supplied to the soil. So that zinc must be moved in chain from plants to animals. Urea is the most used macronutrient fertilizer in Pakistan .If we augment zinc with urea; it will be the best way to treat zinc deficiency. Farmers will be able to get a economical fertilizer bag. Zinc within the same bag of urea will be cost effective for farmer and efficient method for fertilizer industry. So that is why I am working on the synthesis of zincated fertilizer.

3.1 Objectives:

- To synthesize the Zincated Fertilizer
- To characterize the zincated fertilizer
- To measure the dissolution rate of zincated fertilizer and analyze its dissolution kinetics

Chapter 4

Materials and Methods

In this chapter, Elaboration is on the details of the materials coated on the macronutrient fertilizer, synthesis of zincated fertilizer and technique used for the synthesis of zincated fertilizer.

4.1 Materials

The materials which were used for the synthesis of zincated fertilizer are macronutrient fertilizer urea (Sigma Aldrich), Zinc Oxide (Dae Jung Korea), Honey Bee Wax (grocery store, Rawalpindi, Pakistan), Molasses (Al Moiz Sugar Mills, Unit # 2, Dera Ismail Khan, Pakistan), Gum Arabica (grocery store, Rawalpindi, Pakistan) and Paraffin oil (Dae Jung Korea).Urea the only macronutrient fertilizer which contains highest amount of nitrogen content about 46% .Chemicals are almost of analytical grade to maintain the purity as high as possible.

4.2 Coating Technique for Synthesis of Zincated Fertilizer

Zincated fertilizer was synthesized by rotary drum coating technique. Macronutrient fertilizer was coated with zinc oxide in a rotary drum type sampler. This rotary drum type sampler was regulated by Wise Mix Ball Mill to control the rpm and time interval in which each sample was being coated.

4.3preparation of Sample

Samples were prepared with two different methods.

4.3.1 Method One

First the measured amount of analytical grade granular urea was added into sample bottle. Then the measured quantity of coating chemical zinc oxide and binder into the sample bottle were further added. After that sample bottle was placed on Wise Mix Ball Mill. Sample bottle was vigorously rotated for two hours at the speed of 400 rpm. Then the entire sample from sample bottle was taken out and put it into the

Petri dish. For drying the sample, the Petri dish was put into oven for 45 minutes at the temperature of 43c°.Samples was taken out the sample from oven, when it was completely prepared.

4.3.2 Method Two

Here first the slurry of zinc oxide with binder of desired composition was prepared. Then the measured amount of zinc oxide and binder was added in the beaker. Then the beaker was put on the hot plate and stirred it with the speed of 100 rpm for 5 minutes. When the slurry was fully prepared, the measured amount of granular urea and slurry was added in sample bottle. Then sample bottle was placed on the ball mill. Bottle was rotated vigorously for 1 hour and 45 minutes at the speed of 345 rpm. After taking out entire sample from the sample bottle, I put it into Petri dish and placed the Petri dish in oven to dry it for 30 minutes at 38 c°. When sample was completely dried in oven it was completely prepared.

4.4The composition of binder and coating material in Zincated Urea 1

Table 2 Composition of Binder and Coating Material in Zincated Urea 1

Zincated Urea 1		
Chemicals	Quantity	Percentage
Urea	19.54 gm	97.9%
Zinc Oxide	0.4 gm	2%
Honey Bee Wax + Gum Arabic solution (5% each)	1 ml	--
P-Oil	0.5 ml	--

4.5The composition of binder and coating material in Zincated Urea 2

Table 3 Composition of Binder and Coating Material in Zincated Urea 2

Zincated Urea 2		
Chemicals	Quantity	Percentage
Urea	19.6 gm	98%
Zinc Oxide	0.4 gm	2%
10 ml Solution of (honey bee wax + Gum Arabica(5% each))+1 ml of p-oil+1 ml molasses	1.5 ml	--

4.6The composition of binder and coating material in Zincated Urea 3

Table 4 Composition of Binder and Coating Material in Zincated Urea 3

Zincated Urea 3		
Chemicals	Quantity	Percentage
Urea	19.6 gm	98%
Zinc Oxide	0.4 gm	2%
Solution of Honey Bee Wax +Gum Arabic (5% each)	2.5 ml	

4.7The composition of binder and coating material in Zincated Urea 4

Table 5 Composition of Binder and Coating Material in Zincated Urea 4

Zincated Urea 4		
Chemicals	Quantity	Percentage
Urea	50 gm	98.03%
Zinc Oxide	1 gm	1.96%
Paraffin Oil	1 ml	--
Solution of Honey Bee wax + Gum Arabic (5 % each)	2 ml	--

4.8The composition of binder and coating material in Zincated Urea 5

Table 6 Composition of Binder and Coating Material in Zincated Urea 5

Zincated Urea 5		
Chemicals	Quantity	Percentage
Urea	19.6 gm	98%
Zinc Oxide	0.4 gm	2%
Solution of Honey Bee Wax + Gum Arabica (5 % each)	1.5 ml	--

4.9The composition of binder and coating material used as slurry in Zincated Urea 6

In this recipe first we prepared the slurry of binder with zinc oxide and then we applied it for coating purpose on macronutrient fertilizer. I took 10 ml of solution of honey bee wax +Gum Arabica (5% each).Then further added 2 ml of paraffin oil into it and 2 ml of molasses. After complete mixing I added 2 grams of zinc oxide.

Table 7 Composition of Binder and Coating Material in Zincated Urea 6

Urea	50 gm
Amount of slurry used for coating	3 ml

4.10The composition of binder and coating material used as slurry in Zincated Urea 7

In this recipe first we prepared the slurry of binder with zinc oxide and then applied it for coating purpose on macronutrient fertilizer. First I put 6 ml of molasses in beaker. Then further added 1 ml of paraffin oil into it and 2 ml of water. After complete mixing I added 2 grams of zinc oxide.

Table 8 Composition of Binder and Coating Material in Zincated Urea 7

Urea	50 gm
Amount of slurry used for coating	3 ml

4.11The composition of binder and coating material used as slurry in Zincated Urea 8

In this recipe first we prepared the slurry of binder with zinc oxide and then applied it for coating purpose on macronutrient fertilizer. I put 5 ml of molasses in beaker. Then I further added 1 ml of paraffin oil, 2 ml of solution of honey bee wax + Gum Arabica (5% each) and 3 ml of water into the beaker. After complete mixing I added 2 grams of zinc oxide

Table 9 Composition of Binder and Coating Material in Zincated Urea 8

Urea	50 gm
Amount of slurry used for coating	3 ml

4.12 Characterization of Zincated Urea Samples

4.12.1 Scanning Electron Microscopy (SEM)

The coating of zinc on the surface of macronutrient fertilizer was analyzed by scanning electron microscopy. By using format JEOL and instrument JSM-6490 (Japan) complete topography of zincated fertilizer was investigated. Size of the zinc particles, its morphology, compositional differences, crystalinity in coating and location of zinc particles on macronutrient fertilizer were analyzed by scanning electron microscopy. By using sputtering technique, zincated urea granules were coated by gold before taking measurements. To get the measurements with the variety of magnifications, the applied acceleration voltage was 20 kV. The working distance of 10 mm was maintained.

4.12.2 Energy Dispersive X-Ray Spectroscopy (EDX)

In this technique the X-ray spectrum emitted bombarded on the sample with a beam of electrons to get chemical analysis. All elements from atomic number 4 to 92 can be investigated by using this technique. EDX analyzed the elemental composition of coating on the granules of macronutrient fertilizer. Here not only elemental analysis but also chemical nature of elements were observed. Voltage for elemental analysis is 30 kv. The energy range was 0 to 41 keV.

4.12.3 Dissolution Analysis and Kinetics of Zinc Oxide from Coated Macronutrient Fertilizer

Here, sand columns were constructed to calculate the dissolution rate of zinc from zincated fertilizers. Sand column is perfect to analyze dissolution kinetics because of it provides porous medium. Sand was preferred over soil to avoid the influence of soil on dissolution rate of zinc. Strong bonding of soil particles as compare to sand can have high influence on the dissolution kinetics of zinc. These sand columns were constructed using poly ethylene columns (300mm × 20 mm) and Ottawa pool acid washed sand (size range 100-250 µm).The bulk density of Ottawa pool sand was 1.34 g cm^{-3}. The two caps of each polyethylene column (top and bottom cap) were filled with thin layer of acid washed glass wool to avoid the loss of sand during experiment and to prevent any sort of disturbance. Sand columns were first filled with the 20 gram of acid washed sand. Then 1 gram of zincated fertilizer granules on top of the surface of acid washed sand, and further 10 gram of acid washed sand was poured into the column to cover the zincated fertilizer granules. One millimolar percolating solution of calcium chloride of pH 4 was introduced using Pd pump from the bottom of polyethylene column with a fixed flow rate of 15 Ml h^{-1}.At the top of the sand column, solution was taken using manual collector after every 6 hour for 24 hours. Total zinc concentration in all samples was measured by using Atomic Absorption Spectroscopy. Acid washed wool and acid washed sand were used to avoid any contamination or chemical reaction which may affect the dissolution kinetics of zinc. Dissolution Kinetics of zinc in all zincated fertilizers was completely investigated[75].

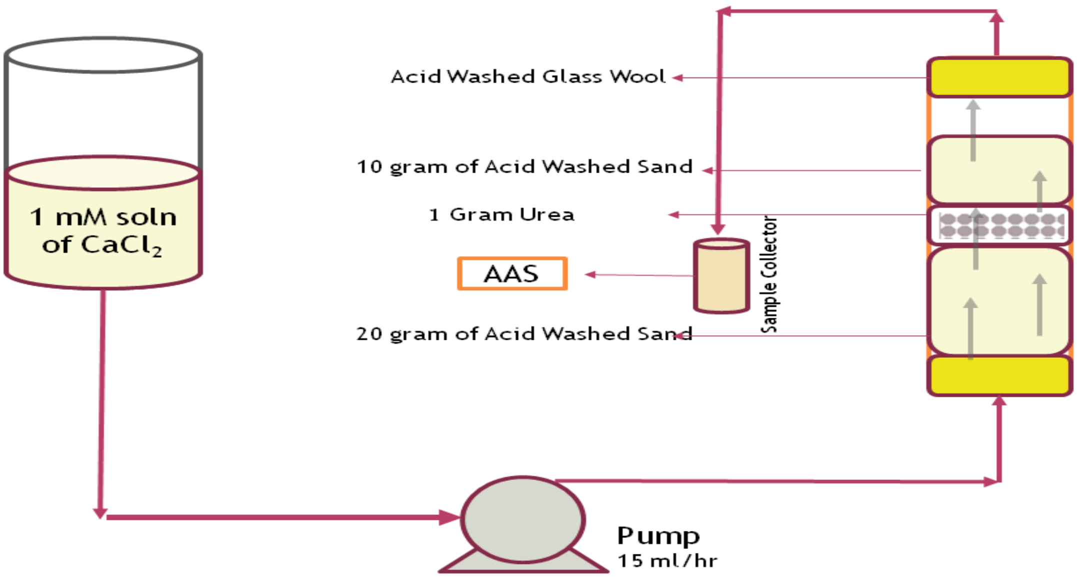

Figure 2 Method used to Calculate Release Rate of Zinc

4.12.4Atomic Absorption Spectroscopy

It is a technique of analytical chemistry, which can measure the concentration of any specific element in a sample to be investigated. Sample may be in a solution form or in a solid form. Atomic Absorption Spectroscopy can determine the concentration of over seventy elements especially in the areas of pharmacology and biophysics. It helps to analyze the elements in the biological fluids for clinical analysis. When the amount of zinc was measured to investigate the dissolution kinetics, the detection limit of instrument was 0.0250 and the reference method was APHA21 1_{st} Edition Method.

Chapter 5

Results and Discussions

In this chapter, the results and facts collected by using different analytical techniques will be discussed.

5.1 Morphology of uncoated granules of macronutrient fertilizer

Before analyzing the morphology of zincated urea samples, first the morphology of uncoated granule of macronutrient fertilizer was analyzed. To study the morphology of pure or uncoated granule Scanning Electron Microscopy techniques were used. In this investigation, Surface morphology was analyzed at x30, x150, x1000, x2000 and x10000 magnification to evaluate structure of the outer layer of uncoated granules. Images obtained at these magnifications show that the surface is plane and there is no particle attached on it. Uncoated granule surface is plane, neat and nothing is present on the outer layer of macronutrient fertilizer[43]. So, when the surface is plane and neat, we don't need any elemental analysis of the layer of uncoated fertilizer[49].

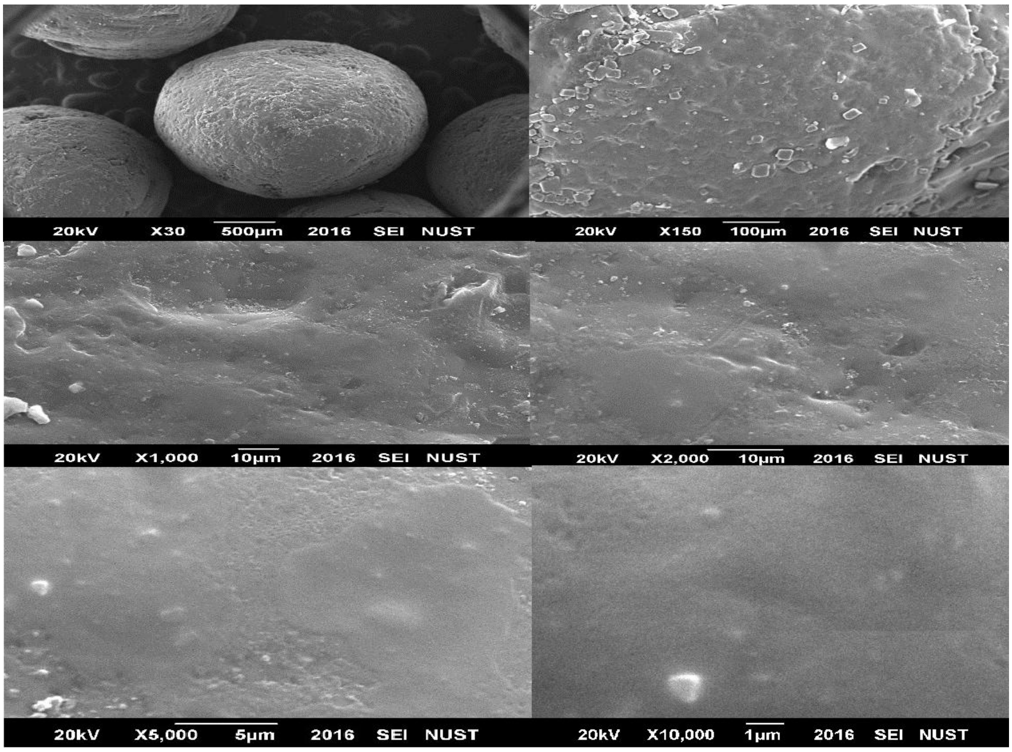

Figure 3 SEM Images of Outer Layer of Uncoated Urea

5.2 Discussion and results of Zincated Urea 1

5.2.1 Morphology of outer layer of Zincated Urea 1

Surface morphology of zincated urea 1 is shown in figure below.At the magnifications of x30 and x150 it can easily be observed that granule is uniformly and properly coated. No Pointy crystals of zinc oxide are present on the surface. There are no gaps or voids on the surface. At higher magnifications X1000 to X10000, pores were still not present, but it can easily be seen the non-uniformity in the size of zinc particles. At higher magnifications it was clearly seen that some particles are lumpy and some are smaller one. This different in size of particles is just because of the binder honey bee wax and gum Arabica solution [1, 8, 16, 18, 27, 62]. Especially Gum Arabica when gum Arabica gets dry it forms crystal like structure and lumpy ones. So to avoid this paraffin oil plays a key role to maintain the uniformity of particles as much as can[67].

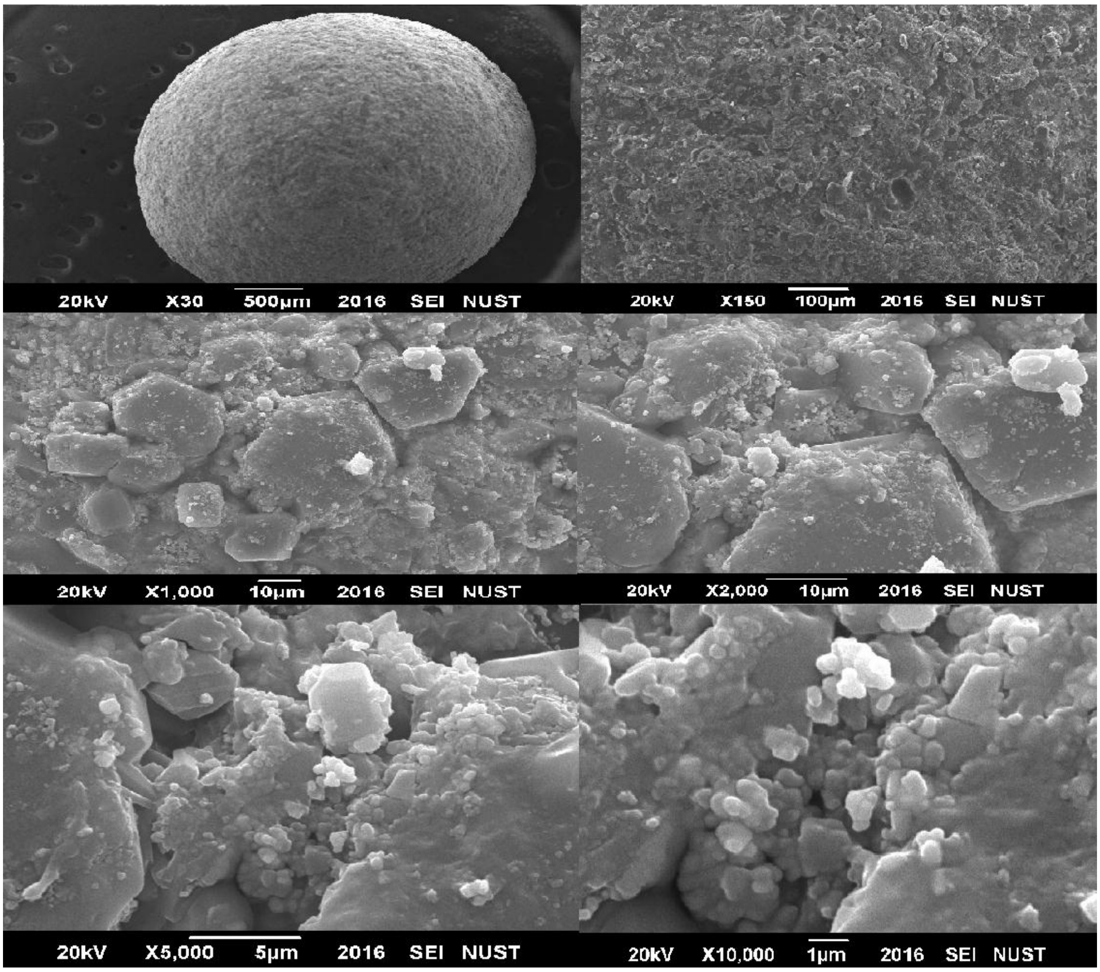

Figure 4 SEM Images of Zincated Urea1

5.2.2Elemental Analysis of Zincated Urea 1 by EDX

According to analysis performed by energy dispersive x ray spectroscopy, Zinc is 83% by mass is coated on to the surface of macronutrient fertilizer. SO the coating as discussed before is very fine.

Table 10 Quantitative Result of Elemental Coating on Zincated Urea 1

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	83.1213	67.9060	0.0757
Si	16.8787	32.0940	0.4935

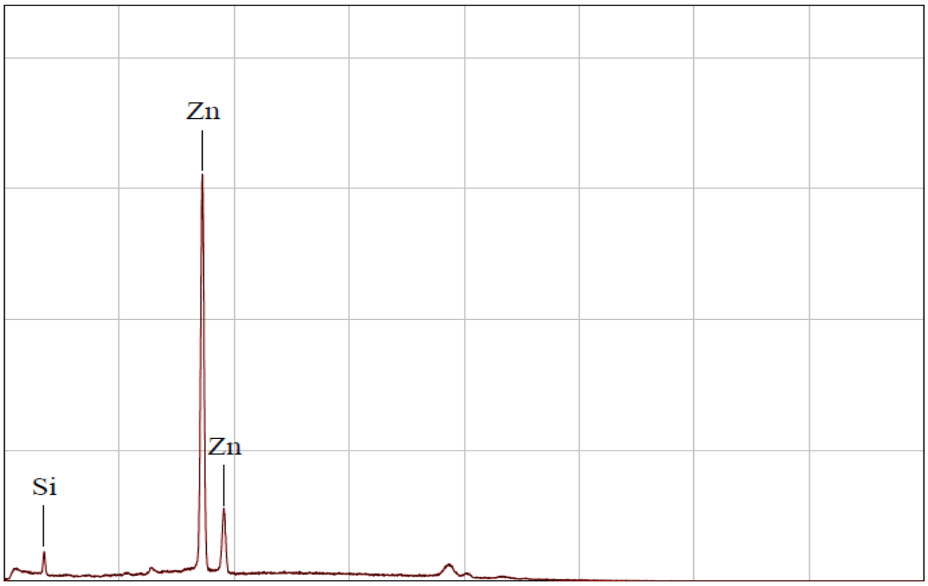

Figure 5 Elemental Analysis of Coating of Zincated Urea 1

5.2.3Dissolution rate of Zinc from Zincated Urea 1

Dissolution rate of zincated urea 1 was calculated after the interval of every 6 hours using sand columns. Concentration of zinc was measured by using Atomic Absorption Spectroscopy. In first eighteen hours there is steep rise in dissolution rate of zinc after that it becomes constant. If we would have further calculated the dissolution kinetics of zinc for more 24 hours, we had reached a point where all zinc got dissolved in water.

Table 11 Release Rate of Zinc in Zincated Urea 1 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	3.019	6
2	7.99	12
3	14.54	18
4	14.172	24

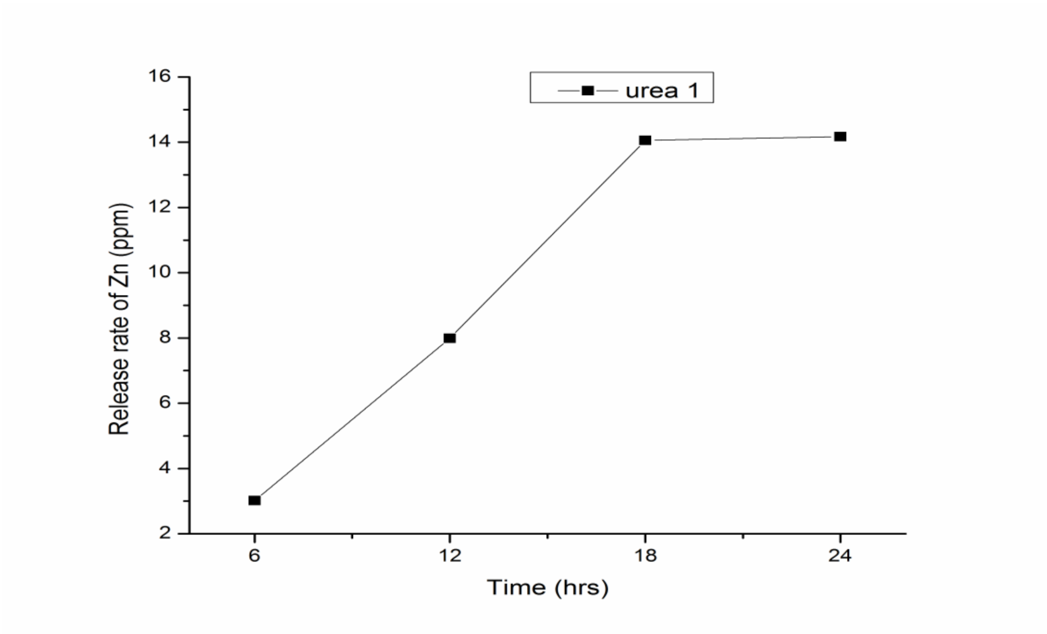

Figure 6 Release Rate of Zinc from Zincated Urea 1

5.3 Discussion and results of Zincated Urea 2

5.3.1Morphology of outer layer of Zincated Urea 2

Surface morphology of zincated urea 2 was quite different from the morphology of zincated urea 1 .At the magnifications of x30 and x150 it can easily be observed that granule is uniformly and properly coated. Although apparently at magnifications of X1000 to X2000 particles looked quite lumpy. But at magnifications X5000 to X10000 beautiful cluster exhibiting zinc structures were easily visible. It can easily be seen the uniformity in the size of zinc particles. There were no voids on the surface. Surface was quite smooth[7]. Addition of molasses in the binder helped in smoother coating of zinc particles. Especially Gum Arabica when gum Arabica gets dry it forms crystal like structure and lumpy ones[11].

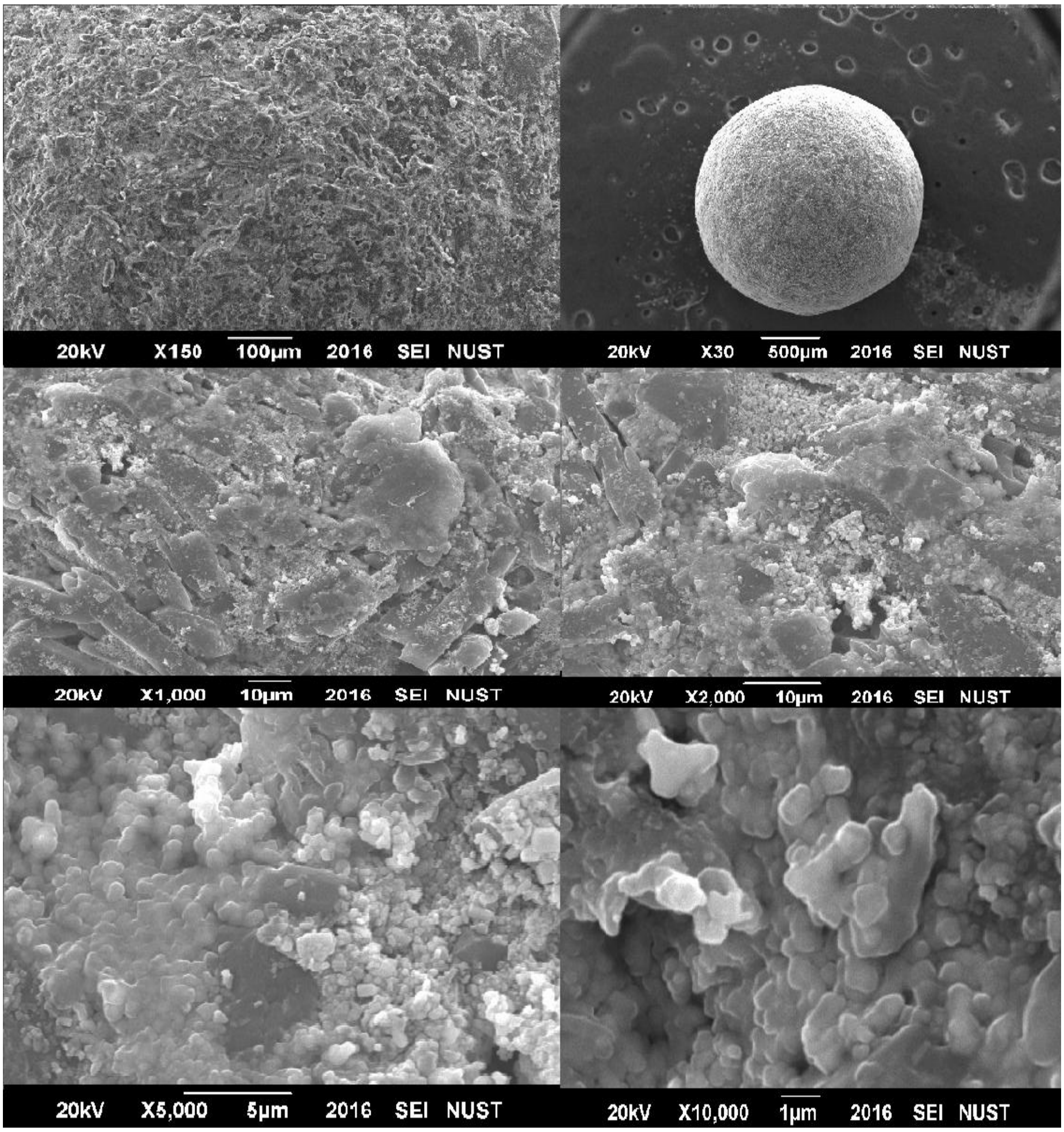

Figure 7 SEM Images of Zincated Urea 2

5.3.2Elemental Analysis of Zincated Urea 2 by EDX

In zincated urea 2, coating efficiency is very good; Zinc is 94% by mass is coated which is comparatively much better than the zincated urea 1.Coating surface is also very smooth.

Table 12 Quantitative Result of Elemental Coating on Zincated Urea 2

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	94.7179	88.5116	0.0758
Si	5.2821	11.4884	0.5012

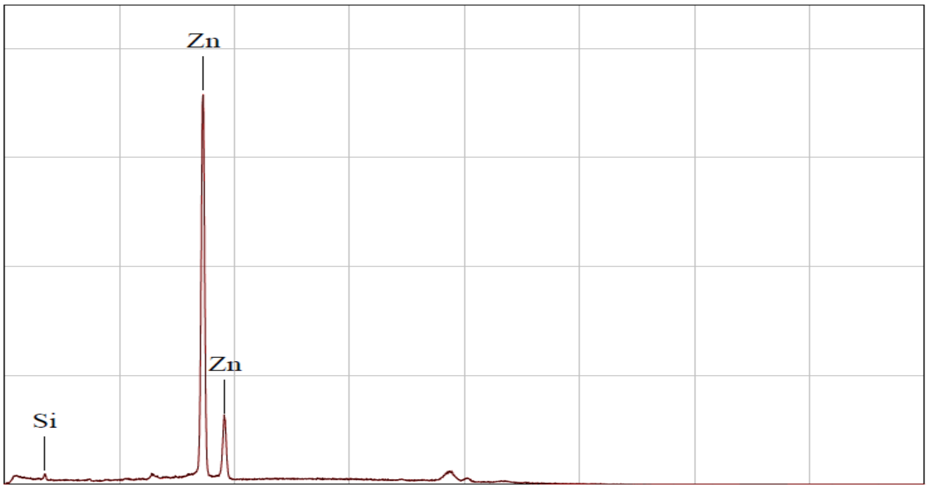

Figure 8 Elemental Analysis of Coating of Zincated Urea 2

5.3.3Dissolution rate of Zinc from Zincated Urea 2

Dissolution rate of zincated urea 2 was also calculated after the same time of interval as of zincated urea 1. Here the release rate of zinc is increasing further with the passage of time but after the eighteen hours steepness becomes less.

Table 13 Release Rate of Zinc in Zincated Urea 2 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	2.81	6
2	8.32	12
3	14.56	18
4	18.02	24

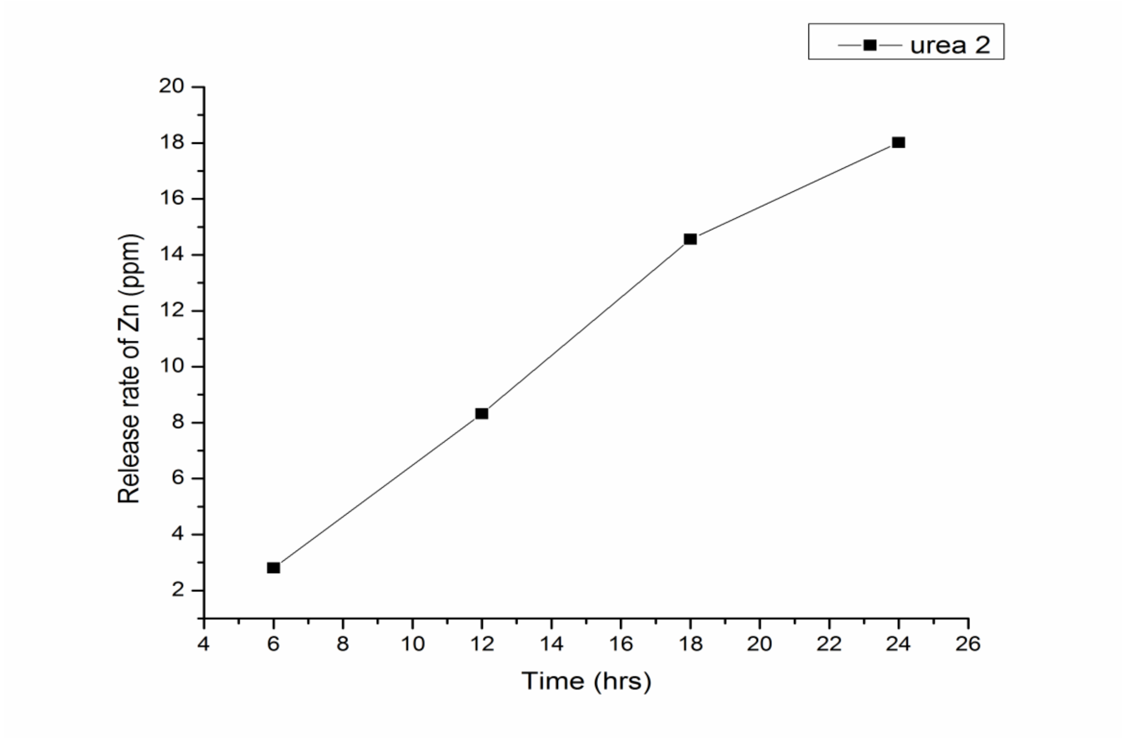

Figure 9 Release Rate of Zinc from Zincated Urea 2

5.4 Discussion and results of Zincated Urea 3

5.4.1Morphology of outer layer of Zincated Urea 3

Surface morphology of zincated urea 3 exhibited most beautiful characteristics ever. Surface of macronutrient fertilizer at the magnifications of x30 and x150 looked very smooth. No voids, no spaces were found on the coating surface. At the magnification of X1000 and X2000, it exhibited pattern of clusters of small zinc particles and large zinc particles [23]. At the magnification of X5000, it exhibited beautiful needle like structure of zinc particles.

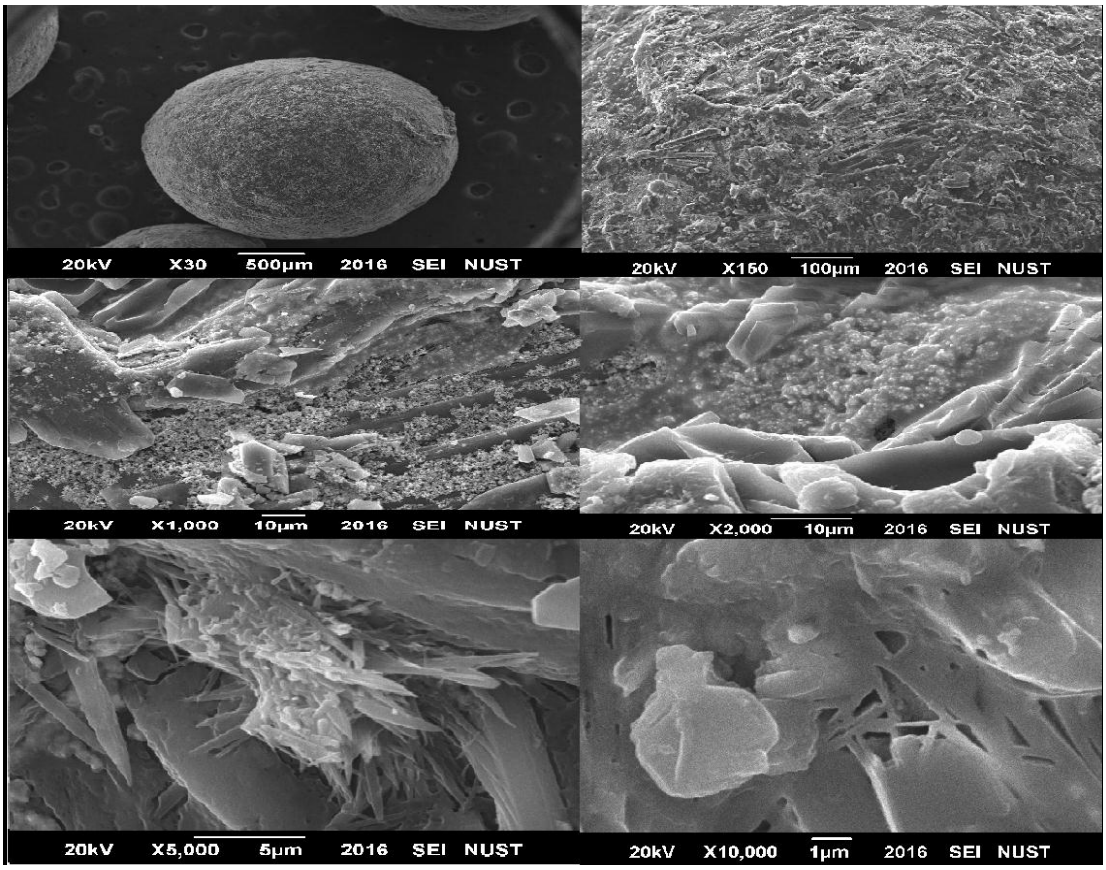

Figure 10 SEM Images of Zincated Urea 3

5.4.2Elemental Analysis of Zincated Urea 3 by EDX

In zincated urea 3, the zinc is 71.5103% coated .Coating efficiency is slightly low but Coating surface is very smooth and exhibit the beautiful patterns of zinc.

Table 14 Quantitative Result of Elemental Coating on Zincated Urea 3

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	71.5103	53.1592	0.0788
Si	19.6262	33.9574	0.5043
Ca	2.3072	2.7974	0.1746
Fe	1.8498	1.6096	0.0444
Al	4.7065	8.4764	0.5439

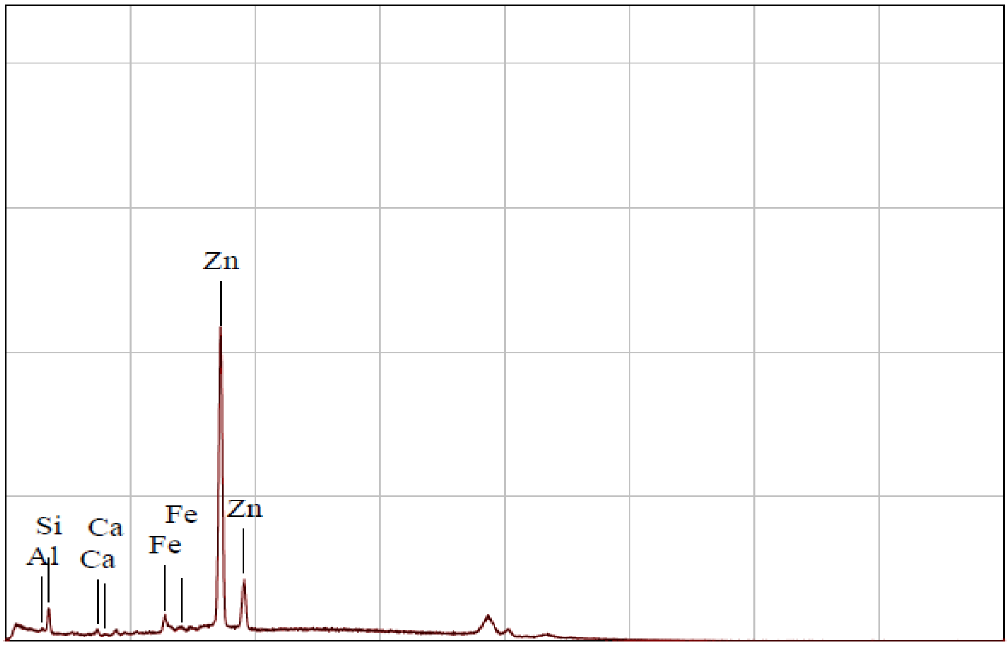

Figure 11 Elemental Analysis of Coating of Zincated Urea 3

5.4.3 Dissolution rate of Zinc from Zincated Urea 3

Dissolution rate of zincated urea 3 is very slow. After 12 hours steepness becomes less but after 18 hours it rises further. In this sample release rate of zinc is very slow.

Table 15 Release Rate of Zinc in Zincated Urea 3 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	3.46	6
2	6.89	12
3	7.79	18
4	9.87	24

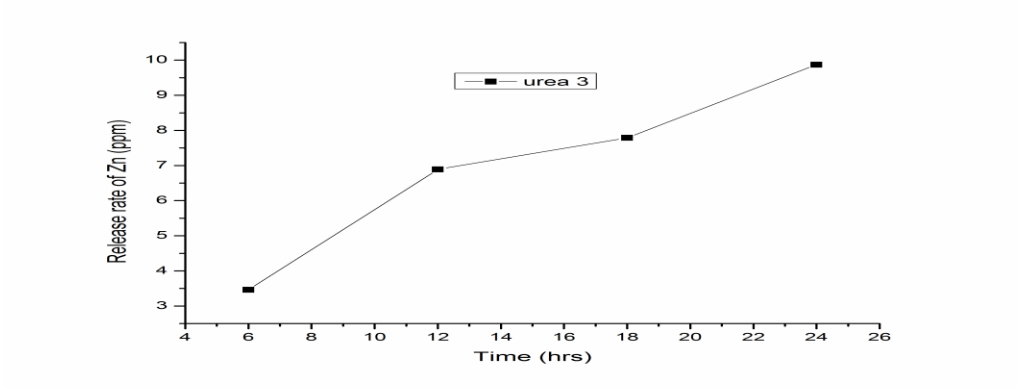

Figure 12 Release Rate of Zinc from Zincated Urea 3

5.5 Discussion and results of Zincated Urea 4

5.5.1 Morphology of outer layer of Zincated Urea 4

Surface morphology of zincated urea 3 was as usual smooth and uniform as of other samples. At X30 and X150, we could easily asses about smoothness and uniformity. But at X5000 and X10000, we observed that zinc was present in very small nanoparticles of 25 nm to 30 nm and large lumps of 150nm to 200nm.

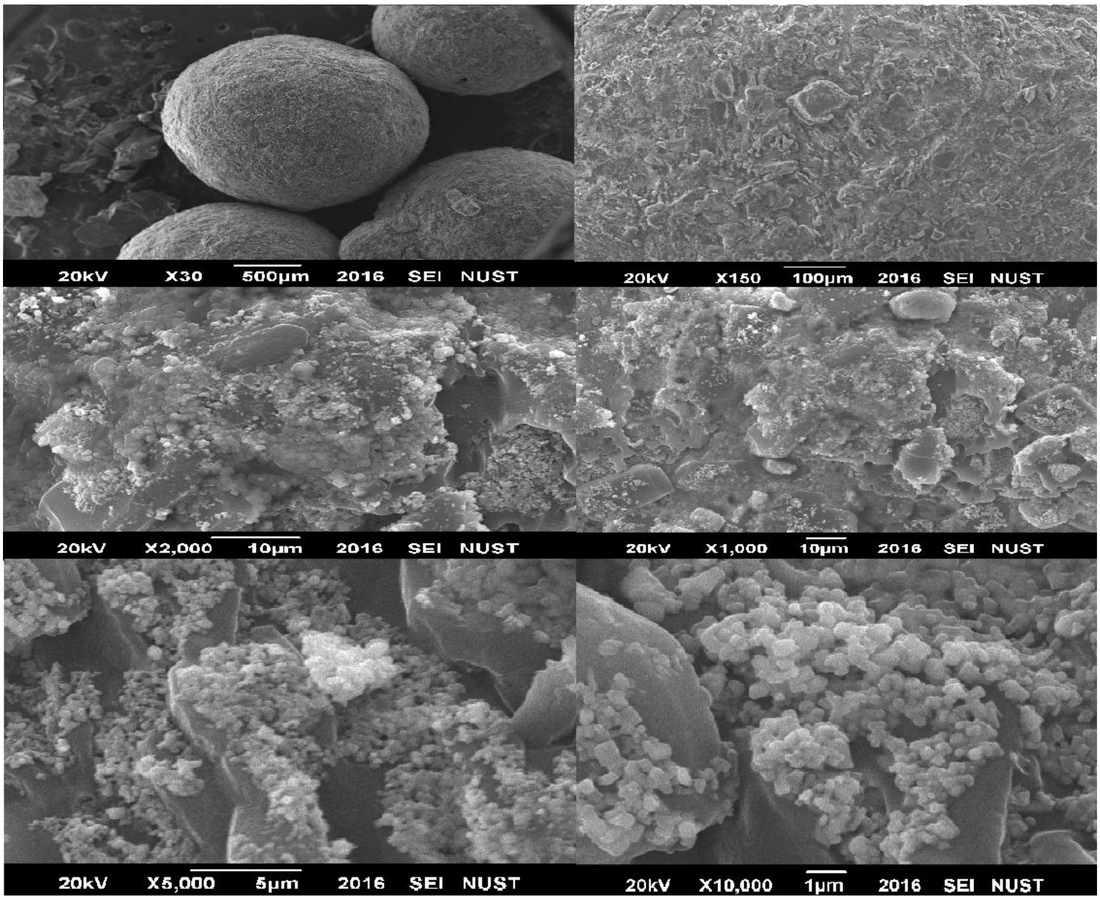

Figure 13 SEM Images of Zincated Urea 4

5.5.2 Elemental Analysis of Zincated Urea 4 by EDX

In zincated urea 4, the zinc is 77.5425% coated .Coating efficiency is better than zincated urea 3 but Coating surface is very smooth.

Table 16 Quantitative Result of Elemental Coating on Zincated Urea 4

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	77.5425	61.6705	0.0737
Si	19.5815	36.2470	0.4608
Fe	1.4480	1.3480	0.0397
Ru	1.4280	0.7346	0.9811

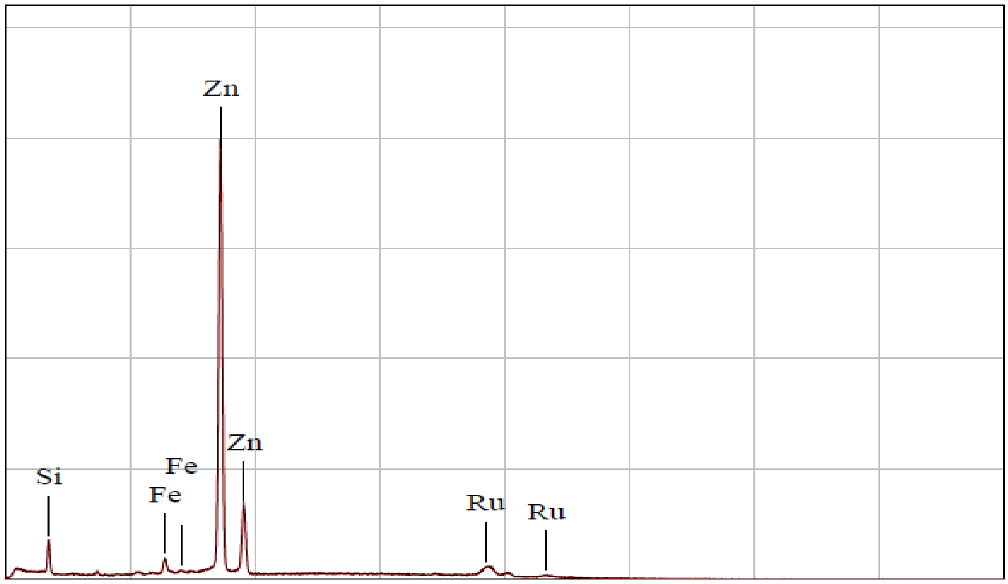

Figure 14 Elemental Analysis of Coating of Zincated Urea 4

5.5.3 Dissolution rate of Zinc from Zincated Urea 4

Dissolution rate of zincated urea 4 is fast. After initial 12 hours the release rate of zinc is very high .Then 12 to 18 hours release rate increases but not with that speed as it was before. From 18 to 24 hours decline in release rate occurred.

Table 17 Release Rate of Zinc in Zincated Urea 4 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	1.89	6
2	12.34	12
3	15.79	18
4	14.12	24

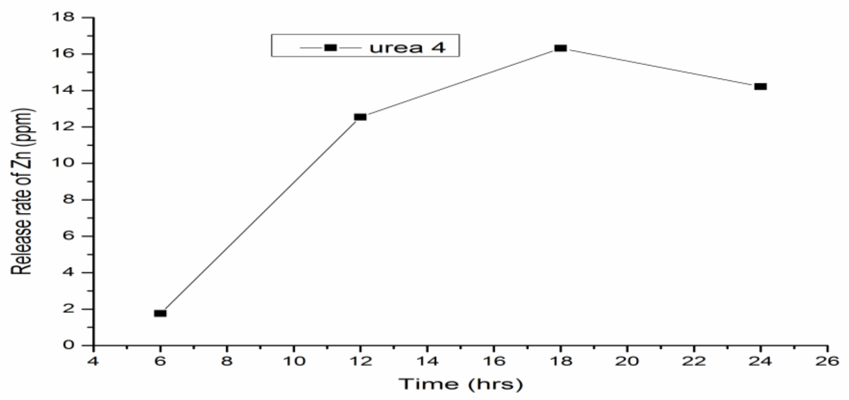

Figure 15 Release Rate of Zinc from Zincated Urea 4

5.6 Discussion and results of Zincated Urea 5

5.6.1 Morphology of outer layer of Zincated Urea 5

Zinc oxide was properly coated and no gaps were found on the surface. At the lower magnifications no lumps are visible. As the magnification increased from X1000 to X10000, big lumps of zinc oxide particles were visible[43]. Although these lumps apparently looked very big but when size was measured, they were not much bigger than 200 nm. Gum Arabica and Honey bee Wax solution (5% each), when used as a binder had the ability to form big lumps of fine particles due to adhesive nature. When these clusters dried, they appeared as big lumps [27, 67].

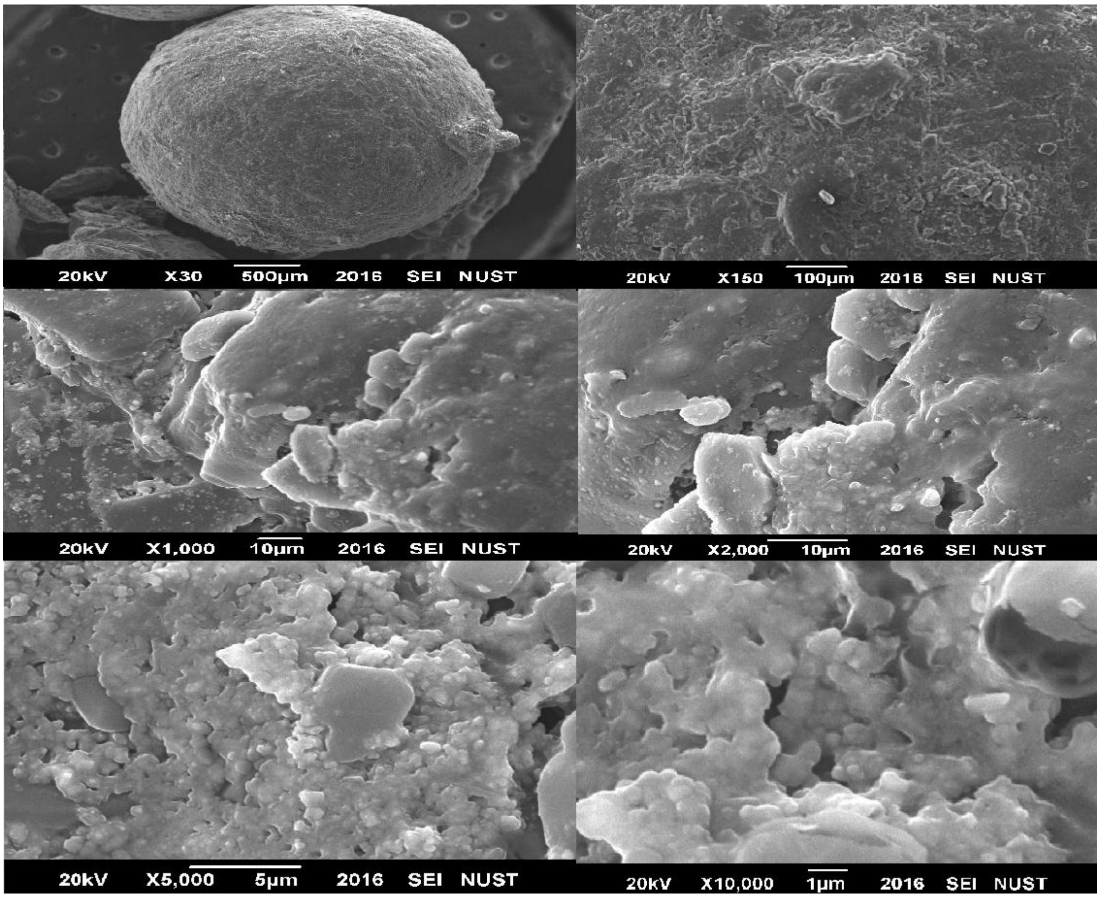

Figure 16 SEM Images of Zincated Urea 5

5.6.2Elemental Analysis of Zincated Urea 5 by EDX

In Zincated Urea 5, the coating efficiency is very high. More than 98% of zinc was being coated on the surface of granule. But the coating was so much crunchy and very hard.

Table 18 Quantitative Result of Elemental Coating on Zincated Urea 5

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	98.0844	95.6521	0.0667
Si	1.9156	4.3479	0.4434

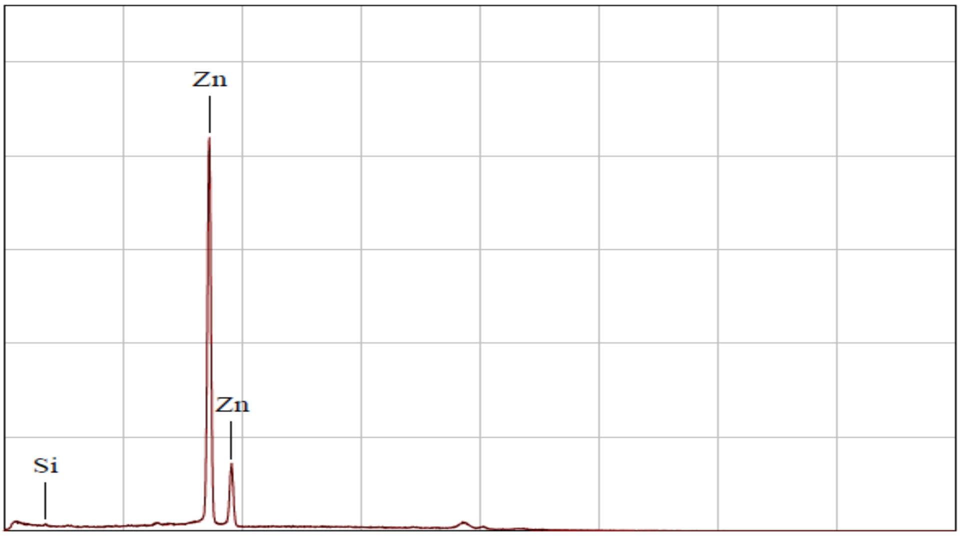

Figure 17 Elemental Analysis of Coating of Zincated Urea 5

5.6.3Dissolution rate of Zinc from Zincated Urea 5

Dissolution rate of zinc in Zincated Urea 5 was the slowest of all samples. Here zinc release rate was very low. Due to crunchy and hard nature of coating on the surface allowed very minute amount of zinc to be released in 24 hours.

Table 19 Release Rate of Zinc in Zincated Urea 5 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	1.932	6
2	2.64	12
3	2.845	18
4	2.978	24

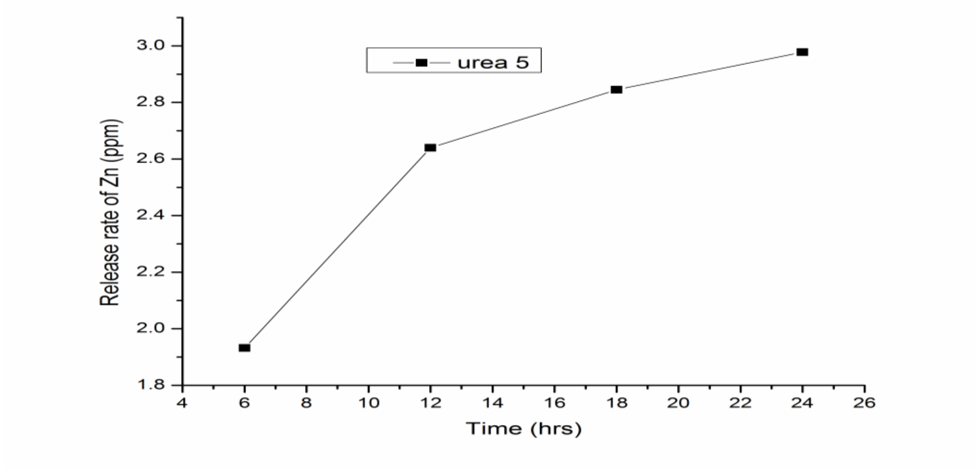

Figure 18 Release Rate of Zinc from Zincated Urea 5

5.7 Discussion and results of Zincated Urea 6

5.7.1 Morphology of outer layer of Zincated Urea 6

Surface morphology was very smooth. Coating was very smooth and soft. No lumps were observed. Granule at the magnification of X30 and X150 looked like surface which was already part of the granule, not the skin on the granule. But at the magnification of X5000 and X10000 small tablets like structures of very fine nanoparticles (size of below 50 nm) of uniform size were visible.

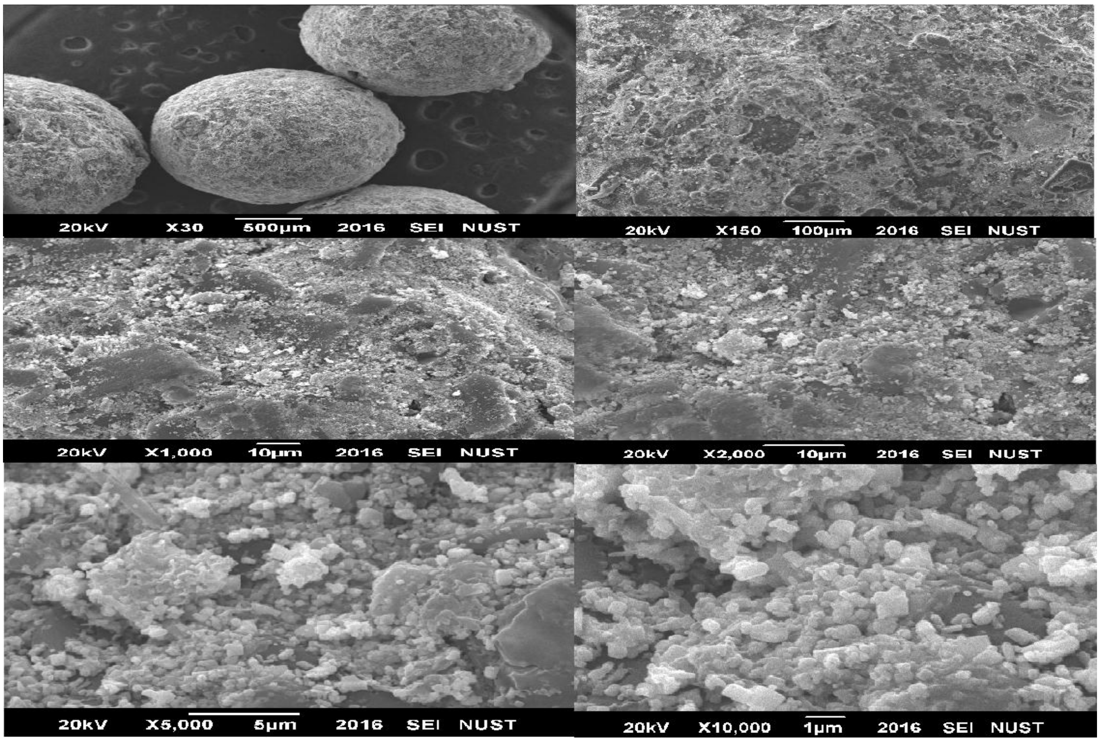

Figure 19 SEM Images of Zincated Urea 6

5.7.2 Elemental Analysis of Zincated Urea 6 by EDX

In Zincated Urea 5, the coating efficiency is very high. More than 98% of zinc was being coated on the surface of granule. But the coating was so much crunchy and very hard.

Table 20 Quantitative Result of Elemental Coating on Zincated Urea 6

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	93.0899	87.9789	0.1225
Si	4.0027	8.8047	0.7746
Fe	2.9074	3.2164	0.0577

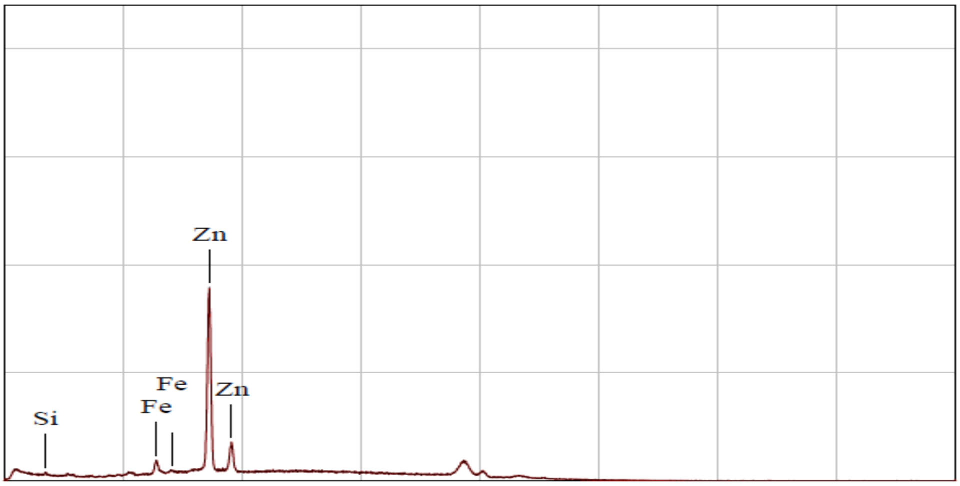

Figure 20 Elemental Analysis of Coating of Zincated Urea 6

5.7.3 Dissolution rate of Zinc from Zincated Urea 6

Dissolution rate of zinc in Zincated Urea 6 was quite fast. In this sample release rate of zinc increased very steadily. Release rate increased steadily after every 6 hours.

Table 21 Release Rate of Zinc in Zincated Urea 6 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	3.87	6
2	5.90	12
3	8.76	18
4	10.11	24

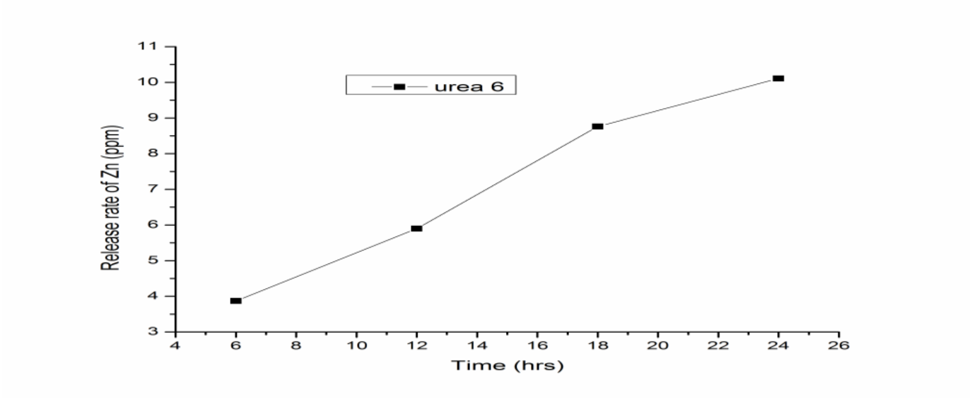

Figure 21 Release Rate of Zinc from Zincated Urea 6

5.8 Discussion and results of Zincated Urea 7

5.8.1 Morphology of outer layer of Zincated Urea 7

Morphology of coating of this sample is very great. No lumps were present. Size uniformity was much more. All particles were properly attached on the surface. At lower magnification smooth and properly coated surface was visible. But at higher magnification, beautiful small nanoparticles of zinc in tablet form were observed.

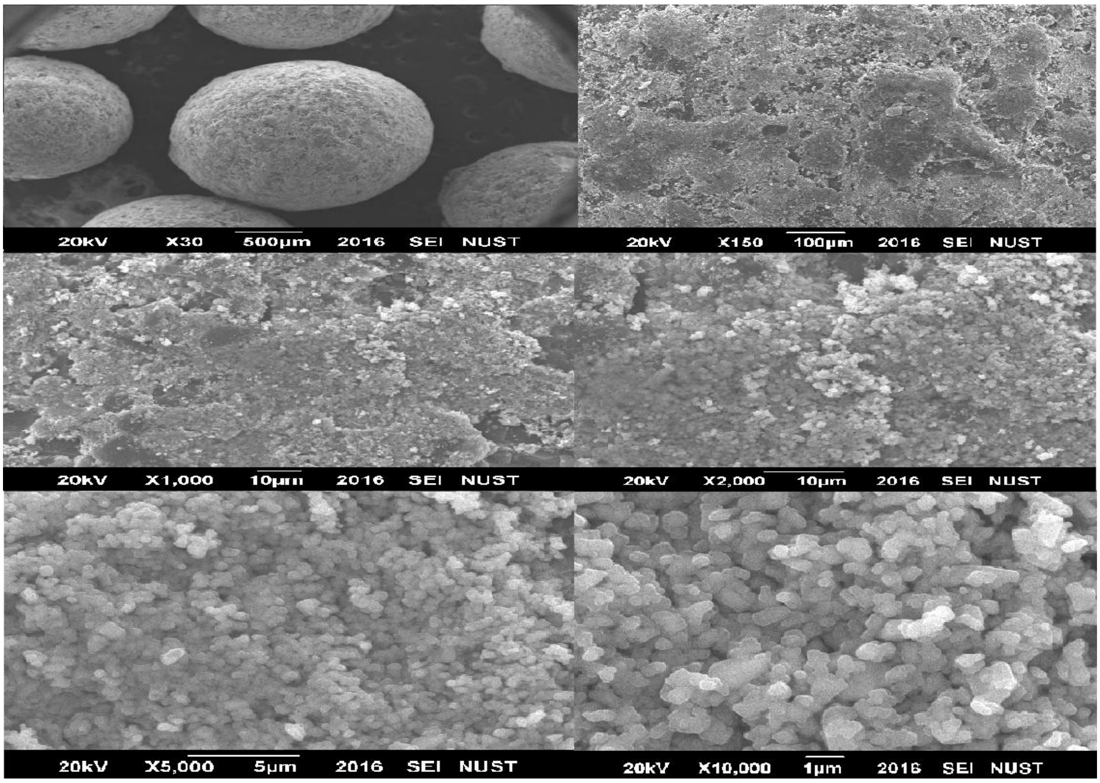

Figure 22 SEM Images of Zincated Urea 7

5.8.2 Elemental Analysis of Zincated Urea 7 by EDX

Zincated Urea 7 was hundred percent coated with the zinc. It was the best sample of all in term of coating efficiency and smoothness[52]. So properly uniform coating was observed. Compression strength was also very good.

Table 22 Quantitative Result of Elemental coating on Zincated Urea 7

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	100	100	0.0695

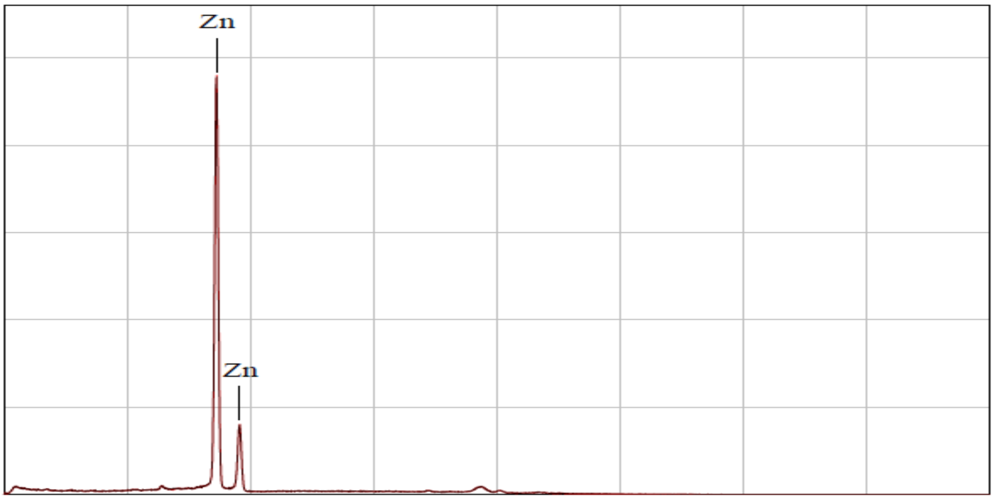

Figure 23 Elemental Analysis of Coating of Zincated Urea 7

5.8.3Dissolution rate of Zinc from Zincated Urea 7

Dissolution rate of zincated Urea was quite steady and uniform[76, 77]. Dissolution rate of zinc was very high. Zinc was being released with accelerating rate.

Table 23 Release Rate of Zinc in Zincated Urea 7 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	3.73	6
2	6.81	12
3	9.02	18
4	12.98	24

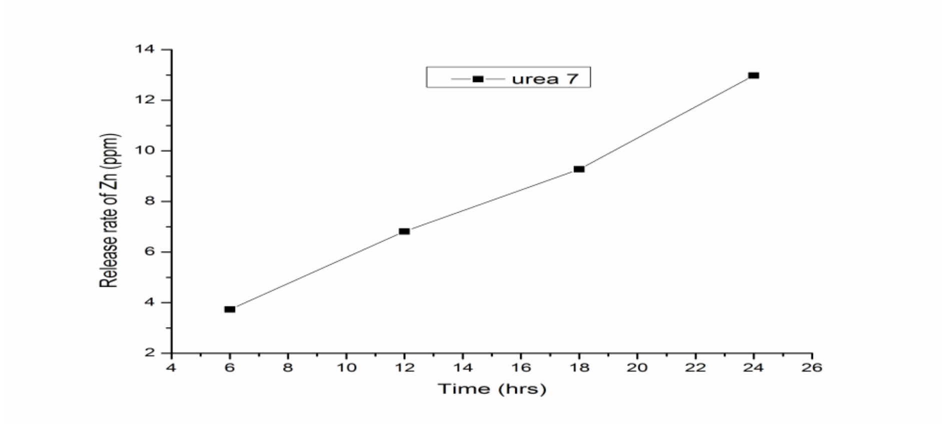

Figure 24 Release Rate of Zinc from Zincated Urea 7

5.9 Discussion and results of Zincated Urea 8

5.9.1 Morphology of outer layer of Zincated Urea 8

Properly uniform coating on the surface of macronutrient fertilizer was observed at the magnifications of X30 and X150. At the magnifications of X5000 and X10000 complete coating was observed, in which lumps were also present. Over all, it was smooth coating, with small lumps on the surface of granule was observed.

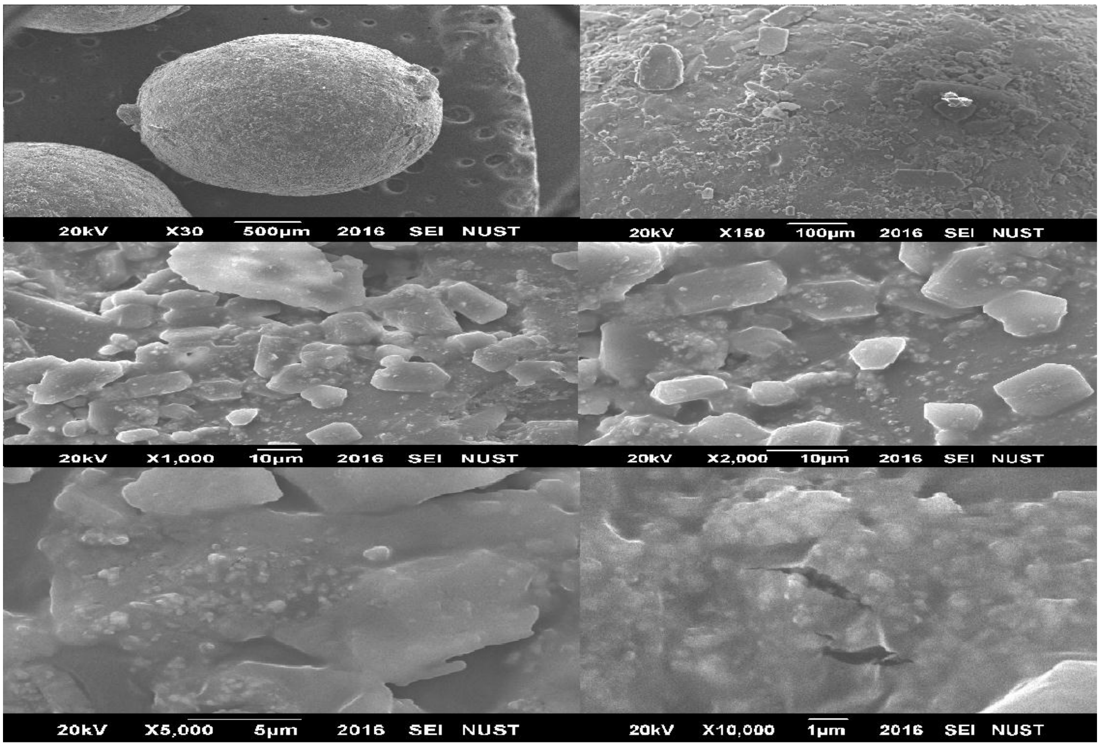

Figure 25 SEM Images of Zincated Urea 8

5.9.2 Elemental Analysis of Zincated Urea 8 by EDX

Zincated Urea 8 was properly coated. Coating efficiency was also good.

Table 24 Quantitative Result of Elemental Coating on Zincated Urea 8

Quantitative Result			
Element	Mass %	Mol%	Sigma
Zn	86.8036	74.7601	0.1939
Si	11.9789	24.0125	0.0964
Fe	1.2175	1.2274	0.1939

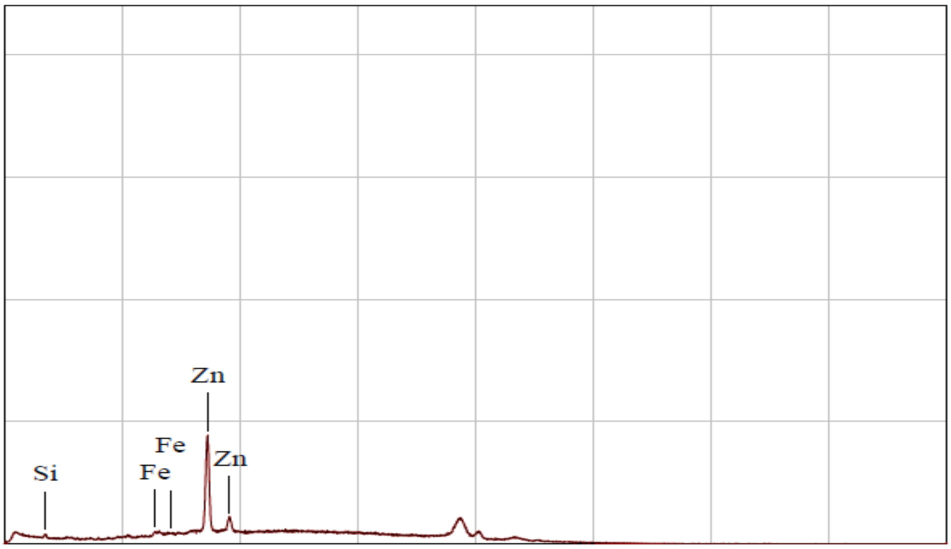

Figure 26 Elemental Analysis of Coating of Zincated Urea 8

5.9.3 Dissolution rate of Zinc from Zincated Urea 8

Dissolution rate of zincated Urea was uniform and fast. The amount of zinc is dissolving very faster. In case we need fast release rate of zinc, this sample can be considered.

Table 25 Release Rate of Zinc in Zincated Urea 8 at Different Intervals

Sr. No	Amount of Zinc (ppm)	Time (hours)
1	1.60	6
2	4.80	12
3	12.69	18
4	17.62	24

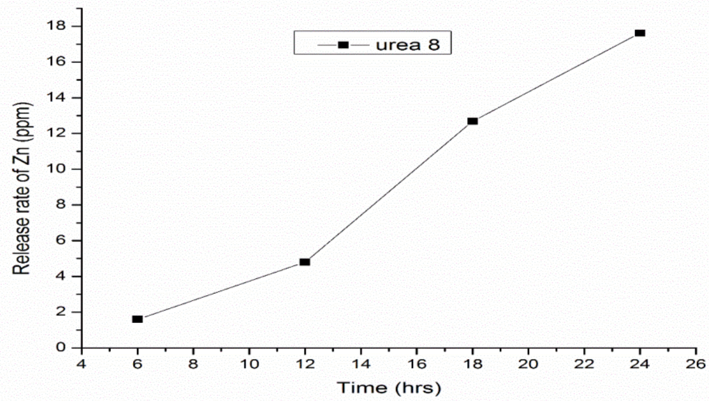

Figure 27 Release Rate of Zinc from Zincated Urea 8

5.10 Comparison in Morphology of all Samples

When we observed the images of all the samples.All th samples exhibited uniform coating at lower magnifications.but at higher magnifications we saw that lumps are being reported in some samples.In all the slurry based coating there were no lumps on the surface of granule.but in non slurry based coating zinctated urea 3 exhibit the beautiful charateristics of zinc at higher magnifications.Zincated Urea 7 was the most best one in term of morphology[8, 22, 36,77].

5.11 Comaprison in Elemental Analysis of Coated ingredients on the Surface of Granule

Coating efficiency of all the samples were very good compared to literature or previous work done so far.Zincated Urea 7 was the most efficient one in which,zinc was hundred percent coated.All slurry based coatings were very fine compare to non slurry based[27].Non slurry based samples exhibited good coating efficiency but not as much efficient as slurry based.

5.12 Comparison in Dissolution Rate of All Samples

When dissolution rates of different samples were analyzed, zincated Urea 4 exhibited the most fast release rate. Zincated Urea 5 showed the slowest release rate of zinc. Zincated Urea 7 release rate was not so fast and not slow. It was the most ideal release rat[75-77].Quite steadily increased with the passage of time.

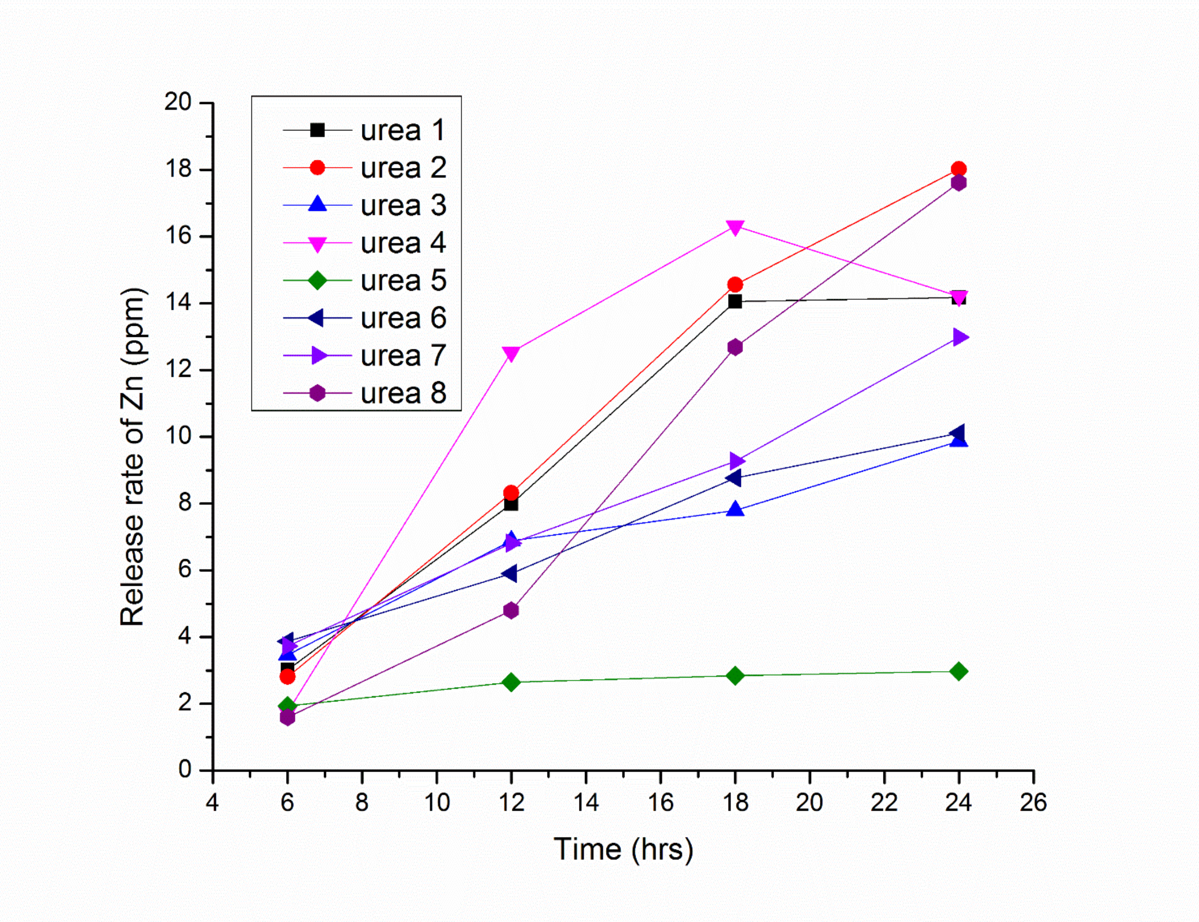

Figure 28 Comparisons in Release Rate of All Samples

5.13 Dustiness

During the packaging and transportation of fertilizer bags, Lot of dust is produced. This dust is normally the upper skin of the surface of the fertilizer granules. So in zincated fertilizer the upper skin is zinc.[5, 19, 37, 42, 65] If upper skin got damaged, the objective of coating would not be achieved. So it is aim that there should be minimum amount of dust during packaging and transportation section to minimize the loss of zinc. So first the zincated fertilizer was heated at 40 c^o. Then fertilizer sample was put in sieve tray and gyrated it for 3 minutes .Before and after hating and gyration, the weight of samples was measured. In this way calculated the dustiness of the samples[77].

Table 26 Percentage Dustiness of All Samples

Sr. No	Weight of sample before heating and gyrating (grams)	Weight of sample after heating and gyrating (grams)	Dustiness %
Zincated Urea 1	12	11.67	2.75
Zincated Urea 2	12	11.77	1.92
Zincated Urea 3	12	11.78	1.84
Zincated Urea 4	12	11.80	1.67
Zincated Urea 5	12	11.73	2.25
Zincated Urea 6	12	11.88	1
Zincated Urea 7	12	11.91	0.75
Zincated Urea 8	12	11.85	1.25

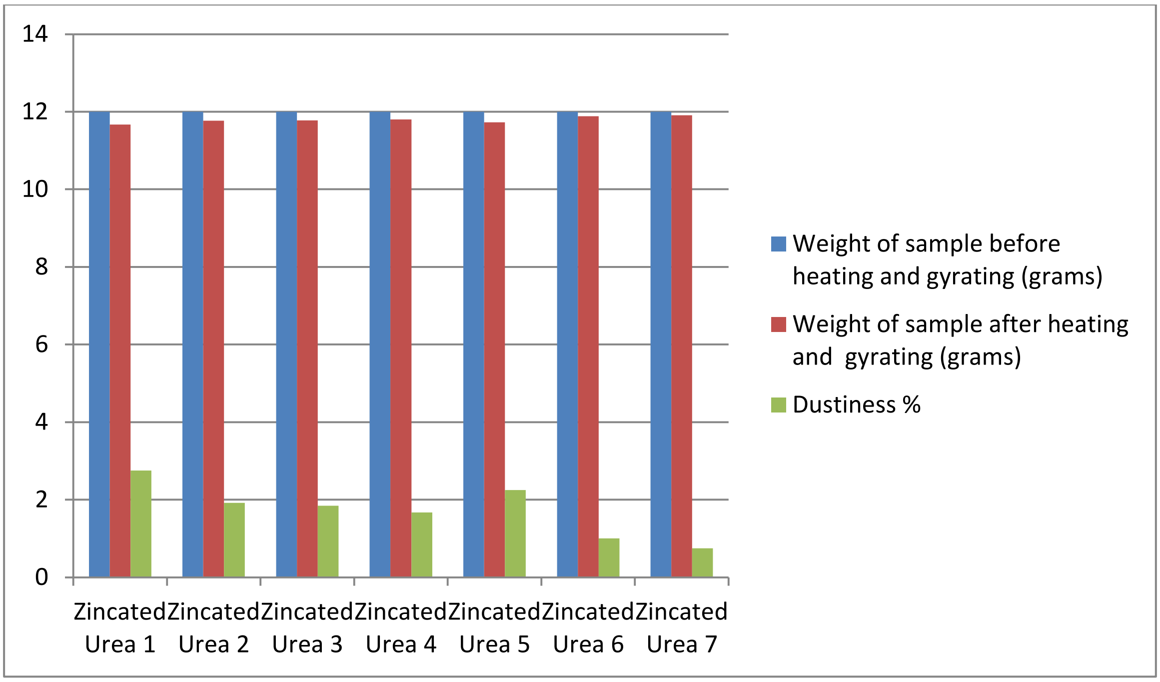

Figure 29 Dustiness

Conclusion

The aim of research was to produce zincated fertilizer. First the finest coating of zinc oxide was developed on the surface of macronutrient fertilizer. The binders which were tried gave very efficient coating of zinc oxide. At lower magnifications, it was all the macronutrient granules were uniformly coated. But at higher magnifications lumps were observed in few samples. But in all samples, which were coated with the slurry. No lumps were observed. Coating efficiency of all samples was very good but slurry based samples were most efficiently coated .Even in zincated urea 7 the coating efficiency was hundred percent. In zincated urea 7, elemental analysis indicated that zinc was the only element on the surface of the granule. Elemental analysis of all samples showed that zinc was in high amount in every coating. After investigation of dissolution kinetics of all samples, we observed that in zincated urea 4, the amount of zinc was dissolved very quickly. Zincated Urea 5 was the slowest of all. But Zincated Urea 7 was quite steady in dissolving the zinc.

Recommendations

This project guides in the preparation of zincated fertilizer:

- By trying new binders, more efficient coating of zinc on the macronutrient fertilizer can be achieved.
- If coating is done in fluidized bed coater, more uniform and efficient coating can be achieved.
- To calculate the dissolution rate, if sand columns were automatically developed then results of release rate of zinc will be finest.
- After getting the release rate, if the order of reaction is calculated. In this way the most accurate release rate of zinc will be obtained.
- If the sand columns parameters will be measured and order of reaction after release rate is calculated. In this way the proper and accurate dissolution technique can be developed.

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Appendices

A. Appendix A

A.1 Basic Definitions

1. Fertilizer

A chemical or a material added to soil to increase its fertility.

2. Macronutrient Fertilizer

Essential components needed by plants for better growth are called macronutrient fertilizer i.e. Nitrogen(N), Phosphorous(P), Potassium(K), Calcium(Ca), Magnesium (Mg) and Sulfur (S)

3. Micronutrient Fertilizer

Trace elements like Boron (Bo), Copper (Cu), Manganese (Mn), Zinc (Zn) and Cobalt (Co) needed by plants for better growth are called micronutrient fertilizer.

4. Zinc Fertilizer

Zinc Sulphate is widely used in soils to overcome the deficiency of zinc.

5. Binder

A substance that is used to attach/mix two or more substances is called binder.

6. Dry Coating

When coating of nutrients on fertilizer is done, without using any liquid moisture as a binder is called dry coating.

7. Wet Coating

When coating of nutrients on fertilizer is done using any liquid moisture as a binder is called wet coating.

8. Slurry or Emulsion Coating

A mixture of coating material and binder used for coating on urea granules.

9. Agglomeration

When different coated urea granules stick together and form cluster is called agglomeration.

10. Crunchiness

Dry hard skin like structure on the surface of macronutrient fertilizer is called crunchiness.

11. Uniform Coating

When all the particles are all of uniform size on the surface of macronutrient fertilizer, it is called uniform coating.

12. Dissolution rate of Fertilizer

The time in which, fertilizer get dissolve in the soil is called dissolution rate of fertilizer.

13. Basic or Calcareous Soil

The soil in which amount of calcium is very high.

14. Coating Efficiency

Percentage of desired coating material on the surface of granule is called coating efficiency

15. Morphology of the Outer layer of granule

The shape of the small particles coated on the surface of granule.

Source: Zinc in Soils and Crop Nutrition

B.J.Alloway

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