

**Development and Characterization Of  
Smart Urea Ionic Co-crystals Fertilizer  
For Controlled Nitrogen Release**



**By  
Mohsin Malik**

**School of Chemical and Materials Engineering  
National University of Sciences and Technology**

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# **Development and Characterization Of Smart Urea Ionic Co-crystals Fertilizer For Controlled Nitrogen Release**



Name: Mohsin Malik

Reg. No: 00000318207

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**Supervisor Name: Dr. Muhammad Bilal Khan Niazi**

**School of Chemical and Materials Engineering (SCME)**

**National University of Sciences and Technology (NUST)**

**H-12 Islamabad, Pakistan**

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# **Dedication**

*Dedicated to my Parents, Teachers and Friends.*

## **Acknowledgement**

Knowledge is scanty to glorify ALMIGHTY ALLAH, The Most Merciful and Beneficent. All praise to Almighty Allah, Lord of the Worlds, The Creator, for providing me the strength, knowledge, potential and opportunity to pursue this research study and to persevere and complete it successfully. Thanks to Almighty, Who is the wellspring of wisdom, and Whose blessing is the treasure of my thoughts. This accomplishment would not have been achieved without His blessings on me. May Allah's peace and blessings be upon the finest of Prophets and Messengers, our Prophet Hazrat Muhammad (PBUH), as well as his family and companions. The greatest social reformer, the source of all knowledge and guidance for mankind, and the cause of the universe's existence.

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## **Abstract**

The world's population is increasing rapidly day by day, leading in global food scarcity. Industrial growth, urbanization, and deforestation, on the other side, will enhance food shortages in most countries. As a result, in the coming decades, considerable rise in mineral fertilizer is expected. The use of normal industrial urea fertilizer has a number of drawbacks, including a number of environmental concerns such as water eutrophication and toxicity, as well as groundwater contamination, environmental pollution, soil quality destruction, and ecosystem disruption.

Fertilizer is vital for boosting soil fertility, enhancing yields, and promoting the quality of the harvest. But unfortunately, a considerable amount of fertilizer is lost, raising agricultural expenses, wasting energy, and contaminating the atmosphere, all of which are major obstacles to modern agriculture's sustainability. For increased crop yield and rapid economic advancement, a consistent, cost-effective, and long-term supply of nitrogen (N) and other plant nutrients is necessary, while maintaining growing population and a good quality of living.

We demonstrate the application of mechanochemistry to obtain control release urea fertiliser in a manner which fulfills the needs of crops as per their growth demands. We conduct urea ionic cocrystal synthesis, incorporating potassium chloride, zinc chloride along with urea nitrate and urea phosphate via stoichiometric reactions in high yields. The resultant materials exhibit distinctive features acquired from the respective inorganic reactants, leading in urea stability with respect to deliquescence in moist conditions by substantially slowing urea hydrolysis in soil, minimizing ammonia emanations & encompassing N accessibility as per crops need.

All the combinations were applied to UV VIS Spectroscopy analysis to check the release of Urea-N from urea ionic c-crystals in comparison with uncoated urea. All urea ionic co-crystals showed the best results for Urea-N release in terms of control release characteristics. Spectroscopy and Crushing strength analysis results revealed that the addition of compacting materials with urea retarded the release rate in water more as compared to uncompact urea. UIC-2 treatment materials crushing strength

was reported as 214.71 N, followed by UIC-3 with 198.36 N. SEM micrograph of UIC-3 showed compacted structure among all combinations.

After the preparation of urea ionic co-crystals pot test experiment conducted using a completely randomized block design with six repetitions on a spinach plant. All soil sampling was done at 0 days and after harvesting of spinach twice (35 days and 65 days).

Plant analysis was conducted after the harvesting of spinach plants. There is no noticeable increase in soil pH. Soil EC enhances after UIC's fertilizer used. Maximum EC was observed in UIC-1 (0.81 dS/m) and the minimum was observed in UIC-2 (0.67 dS/m). TOC value is highest in UIC-3 (8.91 Mg/hac) and less value was shown by UC (7.34 Mg/hac). OM content is highest in UIC-3 (0.77%) and less value was shown by UC (0.63%). Results show that MBC and MBN from UIC-3 treatment are maximum of 175 mg/kg and 93.38 mg/kg respectively, followed by UIC-2 treatment of 147.98 mg/kg and 85.61 mg/kg respectively. MBP and MBK results revealed that treatment UIC-3 shows maximum contents of 23.96 mg/kg and 63.33 mg/kg respectively, followed by UIC-2 treatment of 19 mg/kg and 57.75 mg/kg respectively. In mineral nitrogen UIC-3 and UC treatment represent highest and lowest value of both Nitrate-N and Ammonium-N respectively in both soil and leachate.

Observing the plant analysis, it is observed that in UIC treatment has maximum plant height (23.15 cm and 13.26 cm), plant diameter (2.68 mm and 1.60 mm), leaf area (34601 cm/m<sup>2</sup> and 20623 cm/m<sup>2</sup>), and leaf area index (3.46 m/m<sup>2</sup> and 2.06 m/m<sup>2</sup>) was recorded after both harvestings respectively. Moreover, UIC-3 treatment gave the best result in terms of spinach fresh mass, dry mass yield and nitrogen uptake after both harvestings. From all release rates of fertilizer in water and pot test experiment on plant concluded that UIC-3 fertilizer gives the best result followed by UIC-2 fertilizer.

**Keywords:** Urea Ionic Co-crystals (UIC's), Urea Hydrolysis, Urease Inhibitor, Control Release Urea Fertilizer (CRUF), Spinach, KCl, ZnCl<sub>2</sub>, Urea Nitrate, Urea Phosphate.

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# Chapter 1

## Introduction

Over the previous century, expanded fertiliser, water, and pesticide treatments, combined with modern technologies, have led to huge advancements in modern agriculture. Crop yields per unit land area has gradually upgraded, letting increasing population and has evaluated economic growth [1]. While these changes have been substantial, the environmental consequences have mainly remained unquantified. Overuse of fertilizers and pesticides has resulted in water eutrophication and toxicity, as well as groundwater contamination, environmental pollution, soil quality destruction, and ecosystem disruption, raising concerns about conventional agriculture's sustainability [2-4].

During 1961 & 2001, the world's population has become twice, reaching approximately 6.2 billion from 3.1 billion [5]. After 30 years, this number will have increased to over 9 billion, leading in global food scarcity [6]. Industrial growth, urbanization, and deforestation, on the other side, will enhance food shortages in most countries [7]. As a result, in the coming decades, considerable rise in mineral fertilizer is expected. Mineral fertilizer market rose from 135 million tonnes in 2000-2001 to 185 million tonnes in 2014-2015, with global market expected to exceed 200 million tonnes in 2022-23 [8]. The use of normal industrial urea fertilizer has a number of drawbacks, including a number of environmental concerns. This is indeed an issue that is being debated all across the world. This urea disparity can be reduced by decelerating its dissolution, which can be accomplished through a variety of techniques and methods [9].

### 1.1 Fertilizer

Fertilizer is vital for boosting soil fertility, enhancing yields, and promoting the quality of the harvest. With an estimated nitrogen utilization efficiency of 20-35 percent, emerging nations utilize a significant portion of urea production. But unfortunately, a considerable amount of fertilizer is lost, raising agricultural expenses, wasting energy, and contaminating the atmosphere, all of which are major obstacles to modern agriculture's sustainability [10]. Excessive nitrogen release in the soil is not just



harmful to the environment, but it also affects urea efficiency. Hardly 47% of total fertilizer nitrogen supplied to the environment is consumed by plants, while 40% is lost to the environment and reverted back to unreactive atmospheric dinitrogen, which has a major impact on the overall nitrogen cycle [10].

Fertilizer applications are necessary for intensively high-yield agriculture. Greater fertilizer inputs are required to achieve higher crop yield. These inputs have aided in keeping global food output in line with human population increase, as well as boosting rural economic growth. In modern agriculture, however, misuse of fertiliser, which is provided in excess of plant consumption, is a popular slackness that causes a risk to the environment. Fertilizer efficiency must be considerably raised to avoid harmful environmental implications [11, 12].

## **1.2 Environmental Friendly Fertilizers (EFFs)**

EFFs are a cost-effective solution to improve nutrient efficiency, reduce fertilizer hydrolysis and denitrification losses, and minimize environmental risks. They mitigate pollution caused by nutrient depletion by limiting or even controlling nutrient delivery into the soil [13, 14]. EFFs are typically developed so that fertilizers are bound with environmentally benign materials that decompose in the soil and transform to carbon dioxide, water, methane, inorganic compounds, or beneficial microorganisms. This is the most widely used and available formulation. This is the most widely used and commercially available technique [15].

## **1.3 Nutrients for Plants**

Plants require 16 important and essential plant nutrients to reach their full life span and growth. Crops must have these nutrients in order to grow properly. These nutritious substances are classified into two groups, which comprise mineral and non-mineral group. The 3 elements i.e., Carbon, Hydrogen, and Oxygen, that make up the non-mineral category. Normally, air and water are their primary sources of nutrition. There are 13 elements in the mineral category, that are furthermore categorized into three branches: primary, secondary, and micronutrients, as illustrated in Table. 1.1. [16].

Macronutrients are a form of nutrient which crops require in large quantities [17]. All macronutrients have activities like regulating stem cell osmotic density, protective functions, metabolic activity, and acting as a significant macromolecule and coenzyme

[18]. Micronutrients are those which plants require in extremely tiny quantities. These elements comprise iron, zinc, and boron, among others. In furthermore, larger plants require additional nutrients such as silicon, cobalt, selenium, and sodium [19].

Table 1. 1. Essential Plant Nutrients. [16]

<b>Essential Plant Nutrients (16)</b>			
<b>Mineral (03)</b>	<b>Non-Mineral (13)</b>		
	<b>Macronutrients (06)</b>		<b>Micronutrients (07)</b>
	<b>Primary (03)</b>	<b>Secondary (03)</b>	
<b>Hydrogen</b>	<b>Nitrogen</b>	<b>Calcium</b>	<b>Boron</b>
<b>Oxygen</b>	<b>Phosphorus</b>	<b>Magnesium</b>	<b>Copper</b>
<b>Carbon</b>	<b>Potassium</b>	<b>Sulfur</b>	<b>Iron</b>
			<b>Chlorine</b>
			<b>Manganese</b>
			<b>Molybdenum</b>
			<b>Zinc</b>

Plant parts such as roots, shoots, stems, and leaves utilize a variety of procedures to acquire nutrients from the soil. Although there was a large amount of these nutrients in the soil, the main disadvantage is that just a small amount is easily accessible for crop growth. The effectiveness of crop uptake is determined by the availability and forms of these mineral nutrients. pH, colloids interactions, and the physical character of a soil are some of the additional supporting aspects that influence the uptake mechanism. The acidic or basic properties of soil, as well as its humidity, are key factors. These essential plant nutrients are accessible in all three kinds in soil, i.e. solid, liquefied, and gaseous [20]. Table. 1.2. depicts the key components and their several manifestations.

Table 1. 2. Vital Plant Nutrients And Their Plant Accessible Forms. [20]

Essential Elements	Chemical Symbols	Relative % In Plant To N	Plant Available Form	Functions In Plant
<b>Non-Mineral Elements</b>				
Carbon	C	Are over 90% of total dry matter of plant	CO <sub>2</sub> (g)	Building Blocks Of Macro-molecules.
Hydrogen	H		H <sub>2</sub> O(l) & H <sup>+</sup>	
Oxygen	O		H <sub>2</sub> O(l) & O <sub>2</sub>	
<b>Mineral Elements</b>				
<b>Major Nutrients</b>				
Nitrogen	N	100	NH <sub>4</sub> <sup>+</sup> & NO <sub>3</sub> <sup>-</sup>	Proteins, Amino Acids
Phosphorus	P	6	HPO <sub>4</sub> <sup>+</sup> & H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Nucleic Acids, ATP
Potassium	K	25	K <sup>+</sup>	Catalyst, Ion Transport
<b>Secondary Nutrients</b>				
Calcium	Ca	12.5	Ca <sup>2+</sup>	Cell Wall Constituent
Magnesium	Mg	8	Mg <sup>2+</sup>	Part Of Chlorophyll
Sulfur	S	3	SO <sub>4</sub> <sup>2-</sup>	Amino Acids
<b>Micronutrients</b>				
Iron	Fe	0.2	Fe <sup>2+</sup> & Fe <sup>3+</sup>	Chlorophyll Production
Manganese	Mn	0.1	Mn <sup>2+</sup>	Activates Enzymes
Zinc	Zn	0.03	Zn <sup>2+</sup>	Activates Enzymes
Copper	Cu	0.01	Cu <sup>2+</sup>	Constituent Of Enzymes
Boron	B	0.2	B(OH) <sub>3</sub> (boric acid)	Cell Wall Constituent
Molybdenum	Mo	0.0001	MoO <sub>4</sub> <sup>2-</sup>	N Fixation
Chlorine	Cl	0.3	Cl <sup>-</sup>	Photosynthesis Reactions

## 1.4 Nutrients Loss

Plants can easily obtain nitrogen from urea. The rate of nitrogen release is substantially more as the rate of plant intake. As a result of run-off and leaching from the soil, nutrients are wasted and can't be efficiently consumed by soil and plants [21, 22]. As in transformation of urea to nitrogen, there are two processes: Nitrification and Denitrification, as described in Figure. 1.4-1.

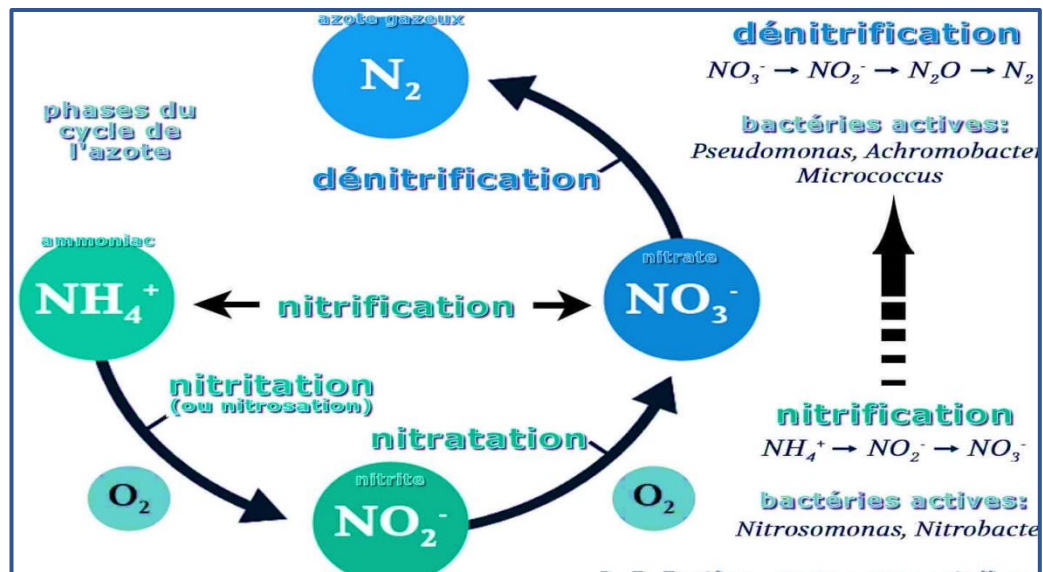


Figure 1.4- 1. Reaction Route Of Nitrification And Denitrification Processes. [21, 22]

## 1.5 Nitrogen Cycle

Nitrogen falls into the class of fundamental nutrients, and it is the primary source of nutrition for all existing species. It is the fundamental component of a wide range of organic chemical substances, including proteins, DNA, and chlorophyll. Having a volume proportion of 78, it is the component of air existing in Diatomic state ( $N_2$ ). This is extremely stable in this state and can be reached by any organism. It is only advantageous for the crops, whenever it is available in the form of  $NH_3$ . The nitrogen cycle is defined as the confined circulation of gaseous nitrogen in a closed loop in which it changes from one state to the other. Plants can produce and utilize nitrogen synthetically in the manner of strongly reactive and water soluble fertilizers [23].

For increased crop yield and rapid economic advancement, a consistent, cost-effective, and extensive nitrogen (N) dispense and further plant nutrients is necessary, while maintaining growing population and a good quality of living [24, 25]. Urea is a

commonly used nitrogen-containing fertiliser developed from  $\text{NH}_3$  and  $\text{CO}_2$ , with an estimated yearly production of 226 million tonnes in 2021 [26].  $\text{NH}_3$  is formed by hydrogenating  $\text{N}_2$  with  $\text{H}_2$  generated from natural gas, a process that utilizes ~1% of worldwide energy and ~4% of total natural gas production [27]. According to Fig. 1.2., once urea is deposited in soil, it undergoes rapid enzymatic dissolution initiated by urease, resulting in a range of N species that can rapidly disperse into the atmosphere instead of being consumed by farmed plants [25].

Urease is an important enzyme found in plants, fungus, and bacteria that relies on nickel and is non-redox. It stimulates urea dissolution at a rate  $10^{15}$  times quicker than that of the non-catalyzed process, making it the most proficient enzyme yet discovered [28]. This reaction, meanwhile, has a lot of agronomic, ecological, and economic consequences [29]. Plants consume only 47% of the total nitrogen provided to soil via fertilizers. [25].

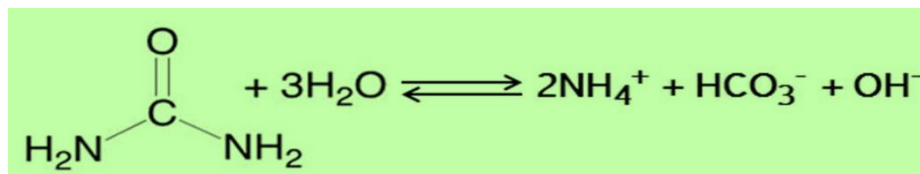


Figure 1.5- 1. Urease Catalyzes The Overall Hydrolysis Of Urea. [27]

## 1.6 Nitrogen Loss From Soil

Nitrogen loss from urea is mainly because to the quick pH rise caused by urea hydrolysis, which is catalyzed by soil urease exercise [30] (see Fig. 1.1.) and results in the escape of gaseous ammonia out from soil [31], which can contribute to more than 90% of the provided fertilizer [32]. Apart from the loss of nitrogen, ammonia is poisonous to plants [33] so has a number of other effects as a result of ammonia nitrification [34] and tropospheric contamination with Nitrogen comprising  $\text{NO}_x$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$  (a GHG about 300 times the heat-trapping capability of  $\text{CO}_2$ ), [35] as shown in Figure. 1.6-1.

The following are two types of nitrogen losses to soil:

1. Permanent Losses
2. Temporary Losses

### 1.6.1 Permanent Losses

Permanent losses comprise those caused by de-nitrification, which involves the transformation of  $\text{NO}_3^-$  to the diatomic nitrogen gas  $\text{N}_2$ . Leaching is also classified as permanent losses when  $\text{NO}_3^-$  is moved downward from the plant's root sector. Volatilization losses from the earth's surface associated to  $\text{NH}_3$ . Key deficiencies included plant uptake & exclusion in harvested parts of the plant.

### 1.6.2 Temporary Losses

Losses that resulted in immobilization for a short period of time. Microorganisms take up nitrogen in this type of system. Second, nitrogen binds to soil particles, resulting in an exchange. Since the nitrogen existing in the soil is easily accessible to plants, these losses are referred to as temporary losses.

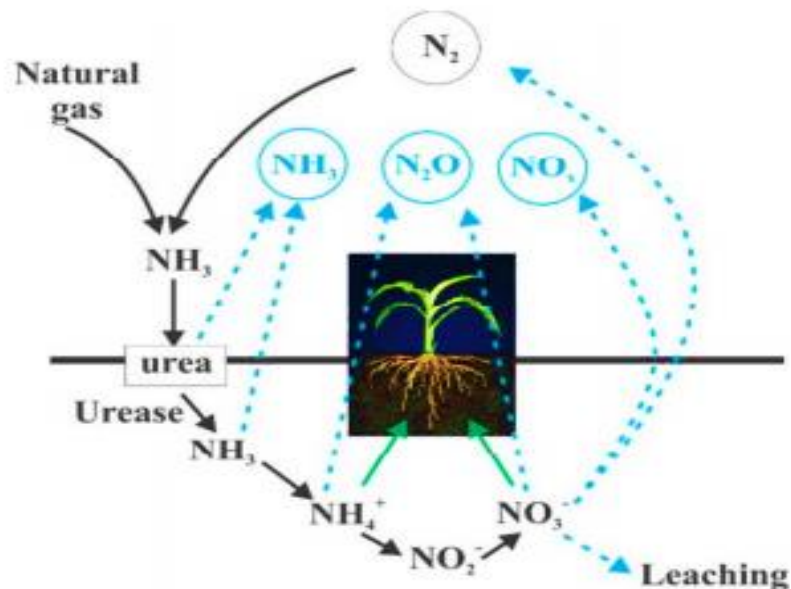


Figure 1.6- 1. Schematic Depiction Of The N Cycle Through  $\text{NH}_3$  Synthesized Utilizing Natural Gas As  $\text{H}_2$  Source And The Resultant Urea Fertilizer. [27]

### 1.7 Slow/Control Release Urea Fertilizers (SRUFs/CRUFs)

Slow or control release urea fertiliser developed in such a way that it meets the needs of crops as per their growth demands. The plant productivity rises as a result of achieving the successive prerequisite [36]. A slow or controlled release urea fertilizer is one that can be produced using a mechano-chemical synthesis approach of a family of urea ionic co-crystals which can utilize as functional fertilizers by substantially

slowing urea hydrolysis in soil, minimizing ammonia emanations, and encompassing nitrogen accessibility as per crops need [25].

A slow release fertiliser is defined as one that meets all three conditions under normal circumstances [22, 37]. The following parameters must be met:

- i. Not over 15% released in 24 hours,
- ii. no over 75% released in 28 days, and
- iii. at least 75% released at the indicated time of release.

## 1.8 Smart Urea Ionic Co-Crystals

Because of diverse accessibility of raw materials, their low prices, and minimal environmental effect, cultivation with minerals and rocks [38] is rising at the frontline of a wide range of options that have been developed for improving the low sustainability of urea use [39]. It doesn't require the application of complicated synthesized chemicals like urease inhibitors [40, 41] despite also providing major nutrients (N, P, and P), secondary nutrients (Ca, Mg, and S), and micro nutrients (Zn, Cl) to the plants. Vivaly, ionic urea co-crystals can promisingly exhibit controlled delivery of major nutrients (N, P, K). For instance, when compacted with urea, salts like KCl and  $ZnCl_2$  have been proven to minimize  $NH_3$  emissions and promote total nitrogen uptake efficiency. The reduction in N losses was between 10 to 20 percent [42, 43]. Though this is a considerable improvement as compared to normal urea fertilizer, an admixture containing both inorganic minerals and nitrogen could provide the benefit of both compounds: vital component nutrition and slow-release characteristics [39]. Recently it was demonstrated that urea ionic cocrystals with Ca and Mg salts can develop through mechanochemical combination and resultantly the ionic cocrystal substantially reduce  $NH_3$  losses [44].

The combination of urea with inorganic salts which can work as both nutrients and urease inhibitors [25] is discussed in this article as a novel crystal engineering strategy [45] to develop urea-based solid fertilizers. Co-crystals, which are generally made up of two or even more neutral ingredients, can be used to achieve a variety of goals in crystal engineering [46-48], since they offer novel approaches to developing and modifying the characteristics of solid active components (compressibility, thermal stability, dissolution rate, solubility, etc.).

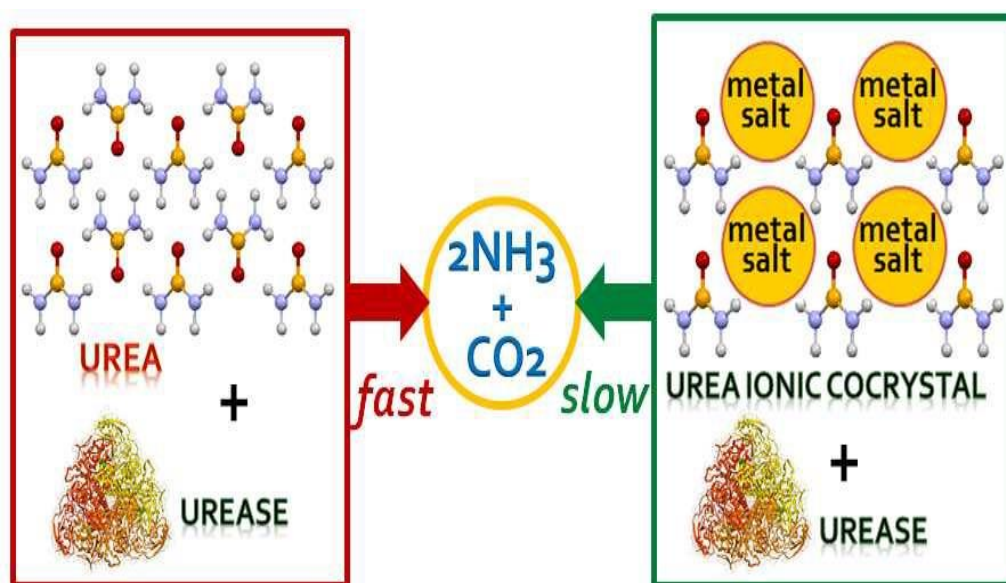


Figure 1.8- 1. Ionic Co-crystals Of Urea With Improved Urease Inhibition. [44]

## 1.9 Ball Milling

Rotary ball mills are well adapted for fine and ultra-fine grinding of tough and rigid materials down to the nanometer size scale [49], for mechanical alloying, and mechanochemical processes because of their large energy density [50-53]. Batch operated circular ball mills are extremely fitted and preferred for use in lab scale processes innovation, due to their high concentrations as well as other advantages (easy setup and operation, ease of maintenance, and low prices) [54].

## 1.10 Mechano Crystal Chemistry

This research is about a two-road intersection. The path of mechanochemistry, that dates back to ancient times and has lately been reintroduced to fulfil the needs for clean operations, environmentally friendly, and solvent-free reactions [55], and the path of co-crystals, that has gained popularity after it has been discovered that many of the core concepts of crystal engineering can be implemented to the creation of such multicomponent advanced materials [56]. Direct mixing, either by the use of a tiny volume of solvent or through mechanical processing of the molecular components, has proved to be a superior immediate and cost-efficient method (no solvent being needed) of preparing molecular and ionic co-crystals [57].



Mechanochemistry is most commonly connected with the breakdown and formation of covalent bonds. The first studies were done using manual grinding or ball milling [55, 58]. Solid-state operations are widely employed in industry, mostly for the production of inorganic solids and materials [59], as well as for the production of amorphous phases [60]. Breakdown and creating noncovalent contacts, which are fundamental for crystal structure and integrity in molecular solids, has been incorporated to the thought of utilizing mechanical means to initiate chemical changes [57].

Co-crystals are multicomponent crystals made up of two or more different chemical substances, each of which exhibits a stable solid state at STP conditions [61, 62]. A multi-component molecular crystal generated by apparently individually stable crystalline or amorphous substances is referred to as a co-crystal. As a result, conventional solvates and hydrates are not considered co-crystals, while co-crystal solvates and hydrates are [57]. Ionic co-crystals (ICCs) produced from an organic molecule and an inorganic alkaline or alkaline earth salt have been synthesized using a mechanochemical technique. Ionic co-crystals integrate the properties of molecular crystals with that of ionic salts (heat resistance, hydrophilicity, etc.) to develop a novel kind of hybrid organic–inorganic co-crystals with new capabilities [57].

Ionic co-crystals are significant subclass of the co-crystal family of compounds [63] that are also actively studied in the search for innovative components for a number of applications (medications, foodstuffs, agricultural chemicals, and optoelectronics) [64]. Latest research has proven that mechanochemically synthesized urea ionic co-crystals using salts can be employed to provide other primary and secondary nutrients, including N, P, K, Ca, Mg, S, Zn, and Cl that are essential for a regulated N intake [65, 66]. As urea is an excellent crosslinking molecule, ionic co-crystals offer innovative strategies to deliver nutrients and fertilizers whilst also resolving the urease inhibition problem.

Here we illustrate this technique by synthesizing a novel ionic co-crystal of urea using KCl and ZnCl<sub>2</sub> along with urea nitrate and urea phosphate, notably urea.ZnCl<sub>2</sub>.KCl (ZnKU), urea.ZnCl<sub>2</sub>.KCl.urea nitrate (ZnKU.UN), and urea.ZnCl<sub>2</sub>.KCl.urea phosphate (ZnKU.UP) via mechanochemical approach [67]. Since nitrogen (N) is required in large quantities by plants and is the primary supplier of protein and

vitamins, potassium (K) is a vital source of plant nutrients, while phosphorus (P) is a compound of cell membranes, proteins, and nucleic acids that is required for a critical response. On the other side zinc (Zn) is both a micronutrient [68-71] and a urease inhibitor [72, 73], the formulation of ZnKU allows for the manufacturing of a material wherein recognized, non-organic, non-toxic, natural mineral-based urease inhibitors can be delivered alongside urea in a single integral crystalline unit, reducing urea solubility in comparison to simple urea. This strategy would additionally be in contradiction to soil zinc inadequacy, which is a key concern in agricultural production [25].

### **1.11 Advantages of Slow Release Coatings**

As smart urea ionic co-crystals based fertilizers are highly effective, operating costs as well as the number of fertilizer treatments to soil are lessened. Slow or controlled-release urea fertilizer is perhaps the most cost-effective and acceptable approach in this case. Several adverse consequences, such as excess fertilization reduced the soil poisonousness as well as seed destruction by the treatment of smart urea ionic co-crystals based fertilizers. The plant's nutrient uptake also boosted by the controlled delivery of nitrogen from described urea synthesis approach. The  $\text{NH}_3$  volatilization emissions attributed with this approach also offer to prevent contamination. This strategy improves handling performance and prevents wastage in the packing and supply chain activities [74]. This boost in effectiveness can be achieved by applying the synthesis method of smart urea ionic co-crystals and lowering the pace at which it is hydrolyzed into the soil. The ionic cocrystals of urea inhibit extra nutrients, and were demonstrated to show enhanced firmness in wet atmosphere. It can be accomplished by an admixture containing both inorganic minerals and nitrogen could provide the benefit of both compounds: vital component nutrition and slow-release characteristics [39]. It has been shown to be a very effective urease inhibitor while also providing soil minerals to enhance N supplies.

### **1.12 Disadvantages of Slow Release Coatings**

Slow-release urea fertiliser synthesis and development is becoming a prominent theme in current times. Slow-release urea fertilizers are not commercially acceptable for a variety of factors, such as non-degradability, that leads to soil eroding and marine pollution. The pH of the soil is influenced by a few slow-release urea fertilizers, which

is damaging for several food-producing plants [75]. Because to particle abrasion, nutritional release occurs earlier than crop's requisite period. The release kinetics of slow release urea fertiliser in interaction with soil and water are the key factors. A alteration in soil characteristics, pH, and the existence of microbes induced this phenomenon [76].

## Chapter 2

### Literature Review

In the preliminary 1960's started controlled-urea research and after then has advanced remarkably [10]. Many substances and compounds have been explored from various indoctrinates of life and proven to help in the steady release of urea as well as provide tangential plant nutrients.

#### 2.1 Ionic Co-crystals Of Urea With Enhanced Urease Inhibition Performance

A smart ionic co-crystal of urea with KCl and ZnCl<sub>2</sub> has been proven to be a very systematic urease inhibitor and has a capacity to provide soil nutrients to accessory N supply. It has been acquired in two polymorphic customization by mechanochemical and solution techniques.

Lucia Casali et al. divulged it in 2018 that through two various perspectives, control of urea durability in fertilized agricultural soils has been trailed. Alteration of urea with urease inhibitors is one of those. By the synthesis of a new ionic co-crystal so called urea. ZnCl<sub>2</sub>.KCl (ZnKU) through both solution and mechanochemical procedures, this approach is manifested by them. The fabrication of a substance in which the supply of known, inorganic and hypoallergenic, instinctive mineral based urease inhibitor as one intrinsic crystalline unit together with urea is enabled by the preparation of ZnKU which consequently reduces the urea solubility with respect to refined urea, as potassium (K) and zinc are essential for plants and inhibition of urease respectively. The inadequacy of zinc in soil is also contradicted by such an approach, which is indicated as a significant issue in crop output.

By the reaction of urea with KCl and ZnCl<sub>2</sub> in 1:1:1 molar ratio, two polymorphic transformations of crystalline ZnKU, form 1 and form 2 have been procured, depending on the devising methods. At room temperature pure ZnKU form 1 is acquired in aqueous solution. Another technique to get it is ball milling. The only technique to obtain refined form 1 from solution is to carry out the reaction and evaporation crystallization at 80 degree Celsius. For the emergence of the metastable kinetic form 1, high temperature is needed and upon sludge in water at RT it is

transmuted into form 2. Pressure is another factor that transforms form 1 into form 2 which is comparatively stable than 1. A dimorphic monotropic system is inaugurated by the two forms of ZnKU. The thermodynamically stable constituent of this system is form 2 whereas form 1 melts at higher temperature than pure urea ( 142 vs 137 degree Celsius). Pragmatic enactment of this crystalline substance requires information regarding mechanical retaliation and the corresponding thermodynamic stability of various forms of ZnKU. The examination of solubility of pure urea versus urea co-solidified in ZnKU has publicized the decrease in urea solubility by about 20% w/v.

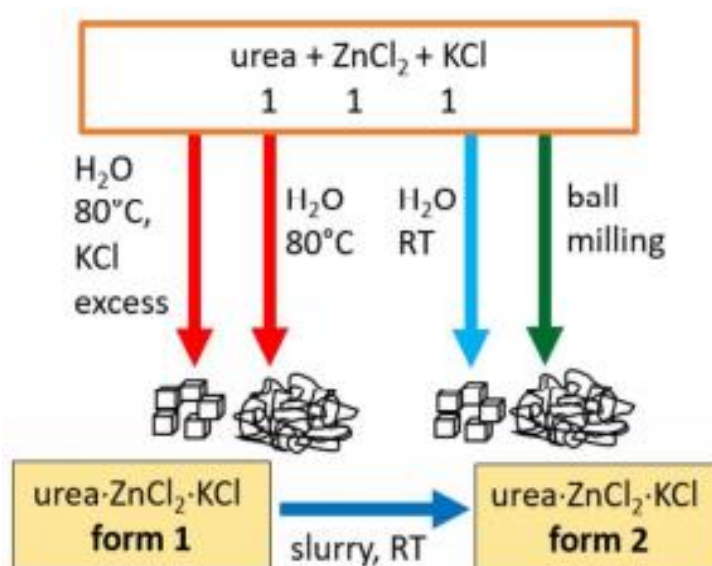


Figure 2.1- 1. ZnKU Forms 1 & 2 Obtained By Reacting Urea, ZnCl<sub>2</sub> And KCl In 1:1:1 Stoichiometric Ratio. [25]

The assembling, delineation and estimation of a versatile substance that is capable of supplying both urea and essential nutrients ( Zn and K) to soil and hampering urease activity to a great extent for enhancing the efficiency of soil N fertilization has been reported by them in this conveyance. In order to raise the inhibition/fertilization duality, the mixture of ZnKU and urea is provided in experiential approach. Multiple aims are executed at the same time by a combination of organic and inorganic pioneers in ionic co-crystals as summarized by them : i) to decrease the release of ammonia in atmosphere develop a sturdy urease inhibitor ii) for crop production impart plant nutrients, and iii) make use of an elementary, statistical, upgradeable and ecological simulated mechanism. It has been manifested by them that the scheme to design crystal can be used to formulate stuff for applications in field of biotechnology and agriculture.

These applications are primarily essential for areas of increasing global significance that are food yield, human sustenance, energy preservation, and environment safeguarding.

## **2.2 Reactive Mechano-synthesis Of Urea Ionic Co-crystal Fertilizer Materials From Minerals With Less Absorption**

To regulate the interweaving of magnesium and calcium- urea ionic co crystals along with their nitrates, sulfates and phosphates in large amount by carrying out balanced chemical reactions between ample minerals having low solubility such as carbonates, oxides and hydroxides and solid urea inorganic acids, the practice of mechanochemistry was illustrated. The eccentric characteristics are shown by the materials resulting from the above mechanism, which they take over from the parallel inorganic reagents and the consequence is balancing of urea with respect to its smoothness in humid environments [39].

The formation of urea ionic cocrystals with salts of magnesium and calcium through mechanochemical coalescence and crucial decrease in the discharge of  $\text{NH}_3$  resulting from ionic cocrystal  $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$  was shown by Honer et al. in 2018.

### **2.2.1 Mechanochemistry And Crystal Structure Testing**

As mechanochemical exploration of solid reagent imparts an extensible, durable and solvent free course of solid-solid transfiguration so it was solicited. An operated state is generated caused by variations in solid structure accompanied by the cautious composure to the equilibrium state during the mechanical inception of chemical reactions. In the transformation of appallingly soluble minerals like oxides of metals into the production of metal-organic substructure, mechanochemistry has been shown to be affluent. Some of the present experiments made use of minute amounts of enumerated liquid  $\text{H}_2\text{O}$  as mechanochemical reactions can be accelerated and validated between solids in a theatrical manner by them particularly while mechanochemistry is contemplated solvent free. A total of 200 mg to 400 mg specimen of Mg or Ca pioneer (carbonate, oxide or hydroxide) urea acid co-crystal (urea phosphate, nitrate or phosphate) and mixture of urea with the equivalent molar ratios was filled into a 15ml untarnished steel along with three isolated 8mm plated steel balls and settled for at least 10 min at a frequency of 26 Hz in a Retsch MM300 mixer mill. That was all done

in a classic approach. With the help of X-Ray diffraction testimony of crystalline nature of all reactants and products was done. Sigma-Aldrich or Fischer Scientific procure the progenitors of calcium and magnesium together with urea sulfate and urea phosphate of analogous category. The synthesis of urea nitrate was brought about using balanced quantitative amounts of nitric acid and urea at 10 degree Celsius in aqueous solution.

To capitulate urea ionic co-crystals from the alkaline (Ca or Mg) low solvability minerals and urea inorganic acid co-crystals ,innovative mechanochemical course is provided by this work. Apart from that solution based techniques have been used for the formation of these ionic co-crystals in which large volume solution manipulating, crystallization and evaporation are required. Urea nitrogen control is enhanced by the deriving nitrates, phosphates and sulfates which also minimize the rate of its decomposition in the presence of water. Urea acid fertilizers produced on an industrial scale abide by high hygroscopicity can be replaced with the fertilizer material obtained as a result. The subsidiary nutrients like sulfur, magnesium, phosphorus or calcium are found in the ionic co-crystals of urea formed in this work. These co-crystals show better constancy in moist air. The main concern of future work will be recognition of reactive intermediates in this precise mechanochemical conversions calcium and magnesium salts having low solvability to urea ionic co-crystals with the help of spectroscopic techniques<sup>69</sup> and estimation of the comparable reaction wavering.

### **2.3 Mechanochemically Synthesized Gypsum And Gypsum Drywall Debris Co-Crystals With Urea**

For the reduction of susceptible N-losses from the mineral fertilizers into the surrounding, modern, economical and durable strategies are required. An affluent mechanochemical preparation of urea co-crystals was illustrated for this purpose having peripheral nutrients sulfur (S) and calcium (Ca) by treating with drywell gypsum waste which is extensively plentiful. Distinctive reactive characteristics are owned by the resulting  $\text{CaSO}_4 \cdot 4\text{urea}$  co-crystal. As concluded from thermogravimetric measurements ,it has a higher urea spoilage temperature of 195 degree Celsius as it renounces the melting of urea at 137 degree Celsius [78].

An exertion in which urea ( $\text{CO}(\text{NH}_2)_2$ , 99.5 %) and calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 99.3 %) powders were utilized together with marketable gypsum

drywall powder was executed by Karolina Barčauskaitė et al. in 2020. In combination with urea- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  having molar ratio of 4, the merging of co-crystals was carried out. The entire weight of raw materials was 1.5 kg. Their blending was done for 45 min at 34 rpm. The fused blend was grinded for 5 h at 60 rpm in a laboratory ball mill. The grinded product was withered at  $50 \pm 5$  °C for one whole day.

The mechanochemical coalescence of  $\text{CaSO}_4 \cdot 4\text{urea}$  from both refined salts and lavish drywell gypsum was shown by them in this task. They also supply a physiochemical essence for the detected agricultural effectiveness of  $\text{CaSO}_4 \cdot 4\text{urea}$  co-crystal. Solitary co-crystal features with postponed or evaded melting alteration in DSC has been manifested by thermal record. In the same way the combination of in situ Raman and DVS data exhibited less tendency of the interaction of co-crystal with water as parallel moisture while in sand discharging experiments a base N losses were detected. For the explanation of the evident permanence of the co-crystal an initial framework was formulated. In order to decompose the co-crystal into the parent compounds an immense obvious thermodynamic barrier is at hand. As contradictory to the typical urea fertilizers, ultimately an included nutrient disposal in soil was quantified for the stacking of same nutrients.

This task has emancipatory nature in its speculatively distinctive procedure of minimizing the loss of N in soil. Urea is presently conducted from it by making use of simulated organophosphorus compounds. These important products will be formed from procedures evolved within by using minerals or waste having nutrients. Both of these sources contain  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - consequently typical N-fertilizer production is consolidated with the durable conception of cultivation with minerals. In order to attain a symbiotic unification a systematic and prevalent drywall gypsum recovering technology with natively eminent productivity and output mechanochemical urea co-crystal formation are merged for this purpose. To legalize almost 700,000 tons of gypsum found in the eastern US from reprocessed drywell this can become a favorable, but presently neglected technology. Ultimately, many factors lead to the durability of this technique. The neglected N-losses would be granted by the usage of co-crystals of urea. The energy required for the Haber-Bosch process would be thoroughly decreased by it. The typical mechanisms for the production of N-P-K fertilizers that take ammonia as a reagent conventionally give rise to 1.4-2.6 kg  $\text{CO}_2$  corresponding per kg



N riveted for the support of this evidence. Contrary to this,  $\sim 0.01$  kW h/kg is needed by a conventional industrial ball-mill which is expressed as 0.005 kg CO<sub>2</sub> comparable per kg solid milled. By the convalescence of urea from wastewater, maintainability increment would arise from (a) decrease of nutrient overflow from ineffective sources of agriculture thus (b) for consideration of such wastewater reduction of power necessities required and substantially (c) with up to 40% more availability of more nutrients to the crops is attained by crucial improve and simplification of conduct operations of ineffective sources.

## **2.4 Mechanochemical Preparation Of Co-Crystals**

Among the presently most smart practices in the field of crystal engineering, the expedition for tidy and green approaches is combined with the exploration of interwoven modern materials by the synthesis of co-crystals through mechanochemistry: at the time of formation of co-crystals the physio-chemical characteristics of the constituents amplify, mingle or modify leading to conclusively enhanced execution, as in the pharmaceutical industry field, where a mechanism to get new articulations and to upgrade the characteristics (compressibility, thermal stability, solubility etc.) is depicted by them. [57].

To attain latest co-crystalline materials, the prosecution of solvent-free mechanochemical reactions have been directed by Dario Braga et al. in 2013. Both features have significant practical intimations, particularly in the field of pharmaceuticals, apart from speculative applicability. Solvent-free methods are commonly economical and have friendly nature to environment, as the issue of discard of solvent is reduced by them, whereas co-crystals might bring about the recognition of new drugs or enhanced properties of occurring APIs as they are captivating new substances. To melt-based or solution techniques, mechanochemistry has been regarded as advantageous as a more effective and common course of action to shield for new co-crystal conformations. The latterly introduced latest approach of ionic co-crystals guarantees the conveyance of compulsive new locations and revolution.

## **2.5 Urease inhibitors**

It was outlined by Martin Trenkel reported [77] in 1997 that a variety of chemicals have been assessed as soil urease inhibitors. Anyhow, the significant demands of

being innocuous, efficient at low concentration, reliable and amicable with urea (solid as well as solutions), ecological and cheaper have been met by hardly some of the examined compounds. Their classification can be done on the basis of their structures and their presumed link with the urease enzyme.

There are four proposed principal categories of urease inhibitors:

- Chemical agents that link with the sulfhydryl groups (sulfhydryl reagents).
- Hydroxamates.
- Agricultural crop safeguarding chemicals.
- Structurally similar forms of urea and corresponding compounds

Perhaps, the most meticulously considered urease inhibitors are N-(n-Butyl) thiophosphoric triamide (NBPT), phenylphosphorodiamidate (PPD/PPDA), and hydroquinone. Inquest and experiential trial has also been conducted with N-(2-nitrophenyl) phosphoric acid triamide (2-NPT) and ammonium thiosulphate (ATS). The structurally similar compounds of urea are the organo-phosphorus compounds. They are some of the most effectual inhibitors of urease pursuit which causes the active site of the enzyme to become blocked.

The manipulation of urease inhibitors added to urea or to UAN solutions enhances their effectiveness and minimizes the evaporation of ammonia by the application of surface on cultivable land, heath and on swamped rice, hence the toxicity of seed-placed urea is reduced. Urease inhibitors propose eminent pliability for the farmer in management of application of urea/UAN to reduce evaporation mislaying. For the regulation of applications of N and to conserve cultivation schemes, more choices are proposed by them. So far, a granular fertilizer is more convenient to control than any other urease inhibitor (Weber et al. 2004b). Presently a liquid or dry form of Agrotain is available which is the sole retailed urease inhibitor. Ammonia losses to the atmosphere are minimized by urease inhibitors from advertise, supreme urea applications (Watson, 2005) particularly where decreased cultivation is brought about. Ammonia released in the atmosphere may be sedimented on water or land which ultimately leads to acidification eutrophication. Nitrate content in plants can be decreased and nutritional quality of vegetables and silage plants can be enhanced by the delay in synthesis of ammonia and later nitrification as with nitrification inhibitors, urease inhibitors.

## Chapter 3

### Materials and Methods

Compacting materials as well as a methodology of compacting to develop controlled release urea fertilizer are enclosed in this section of article. The characterization strategies used to analyze these controlled release urea fertilizers are also addressed. The details of the pot test investigation are also addressed long-windedly.

#### 3.1 Materials

The materials for this work includes Urea (extra pure), along with compacting materials Zinc Chloride ( $ZnCl_2$ ), Potassium Chloride (KCl), Nitric Acid ( $HNO_3$ ) were imported from Sigma-Aldrich along with Urea Phosphate ( $CH_7N_2O_5P$ ) that was imported from MACKLIN. N-(1-naphthyl) Ethylenediamine dihydrochloride (NEDD), Vanadium (III) Chloride ( $VCl_3$ ), Trisodium Citrate Dihydrate, Sodium Nitroprusside, Sodium Hypochlorite, Ammonium Sulfate, Potassium Sulfate, Ammonium Heptamolybdate Tetrahydrate, Potassium Nitrate, Trisodium Phosphate, Sulfanilamide, Phenol, Hydrochloric Acid, Sulfuric Acid, Orthophosphoric Acid, Diphenylamine, L-Ascorbic Acid, Ethanol, Acetone, Chloroform, Sodium Bicarbonate, Potassium Dichromate, Ferrous Ammonium Sulfate, Potassium Antimony (III) Tartrate Hydrate, Sodium Hydroxide, Ammonium Acetate, Copper Sulfate, Tris(hydroxymethyl)aminomethane, Ammonium Chloride, Ammonium Hydroxide, Potassium Dihydrogen Phosphate, Ethylenediaminetetraacetic Acid, Murexide were imported from Sigma-Aldrich. While, Boric Acid, 1,10-Phenanthroline Monohydrate, Acetic acid, Eriochrome Black T, 4-Dimethylaminobenzaldehyde from Daejung Chemicals.

#### 3.2 Ball Milling Technique Of Compaction

A controlled release smart urea ionic co-crystals based fertilizer was synthesized in a WiseMix® Ball Mill purchased from PMI Labortechnik GmbH, Wettingen. The ball mill was operated at standard conditions, sample was loaded into a 1000 ml HDPE bottle together with 8 mm stainless steel balls with balls to sample ratio of 10:1 and grounded for up to 30 to 40 mins at 200-300 rpm in a WiseMix® Ball Mill.

### 3.3 Sample Preparation

The use of mechanochemical processing of solid reactant powders was adopted because it delivers a solvent-free, affordable, and long-term solution for solid-solid conversions [79-81]. A total of 20 g to 40 g sample of KCl, ZnCl<sub>2</sub>, and urea in a molar ratio of 1:1:1, as well as a total of 20 g to 40 g sample of KCl, ZnCl<sub>2</sub>, urea acid cocrystal (urea nitrate or urea phosphate) and urea mixture with the corresponding molar ratios, was fed into a 1000 ml HDPE bottle with 8 mm stainless steel balls and processed in a WiseMix® Ball Mill for up to 30-40 minutes at 200-300 rpm. Table. 3.1. shows the combination of compacting materials used to create urea ionic co-crystals.

Table 3. 1. The Composition Of Compacting Materials.

Name of Materials (molar ratio)	Sample Name		
	ZnKU	ZnKU.UN	ZnKU.UP
Urea	1	3	3
Potassium Chloride	1	1	1
Zinc Chloride	1	1	1
Urea Nitrate	-	1	-
Urea Phosphate	-	-	1

### 3.4 Characterization Of Urea Ionic Co-Crystals

SEM, EDX, FTIR, Crushing Strength, and XRD were used to investigate the simple and ionic co-crystals urea. To inspect the surface structure and morphology, SEM was used. The characterization approach utilized to assess the respective elemental makeup of simple and ionic co-crystals urea was energy-dispersive X-ray spectroscopy (EDX). A Fourier transforms IR spectrophotometer was used to obtain IR spectra in the wavenumber range of 400-4000 cm<sup>-1</sup>. A Universal testing machine (AGX Plus) was used to conduct crushing tests on urea crystals. On an X-ray diffraction equipment, simple and ionic co-crystals of urea were studied using a scan angle extend over from 10 to 90 degrees.

### **3.4.1 Scanning Electron Microscope (SEM)**

The finest characterization approach for assessing the elemental makeup of uncompacted and compacted urea crystals is energy-dispersive X-ray spectrometry (EDX). An elemental examination equipment, the Oxford X-Act-Model 51-ADD007, was used to determine the nitrogen as well as other elemental constituents in urea fertilizer ionic co-crystals. The gold sputtering apparatus rendered the urea ionic co-crystals prills conductive.

### **3.4.2 Energy-Dispersive X-ray Spectroscopy (EDX)**

The surface structure of urea ionic co-crystals specimens was examined using a scanning electron microscope (S-4700 Hitachi, Japan). For comparison, urea particulate without compaction samples were examined prior to urea ionic co-crystals samples. Ion sputtering was used to develop urea ionic co-crystals before the examination. The Ion Sputtering Machine JFC-1500 of JEOL Ltd was used to sputter gold on urea ionic co-crystals. The gold coating on the crystals was applied up to 250 angstroms. With a subsidiary electron locator using a 20 kV accelerating voltage, the sample surface was examined.

### **3.4.3 Fourier Transform Infrared (FTIR) Spectroscopy**

An FTIR Perkin Elmer Spectrum 100 spectrometer was used to perform Fourier Transform infrared spectroscopy of uncompacted and compacted urea crystal combinations. For examination in the range of 400 to 4000  $\text{cm}^{-1}$ , the urea crystals were squashed into powder form. The bonding character and chemical structure related to the outcome of conjoin between several compacted materials chains were evaluated using the Fourier transform infrared absorption spectrum (FTIR) [84]. For the spectroscopy, potassium bromide pellets were manufactured with urea powder.

### **3.4.4 Crushing Strength**

The aim of crushing strength analysis is to guarantee that the urea crystals can sustain from the production stage to the marketing and selling phase. The urea crystals begins to crumble and transform into particulates as a result of intense physical assaults. Urea Dust is the term for these particulates, and they are no longer useful. A Universal testing machine (AGX Plus) was used to conduct crushing experiments on compacted urea crystals. Compacted urea crystals were chosen at random from the sample set.

The urea crystals were interacted with a metal pusher vs a determined level of stress during the experiment. The rigidity of the urea crystals was evaluated by the force at which they cracked. Usually, this experiment was carried out on the larger granules [82].

#### **3.4.5 X-Ray Diffraction (XRD)**

X-ray diffraction (XRD), of uncompact and compacted urea crystals was carried out by equipment STOE Germany. XRD was done to check Crystallinity of all products developed [44]. Scan angle was from 10° to 90°. Step size and step time were taken as 0.4 degrees & 1 second respectively. Radiation used for depiction was of Cu K  $\alpha$ -1 [85].

### **3.5 Release Rate Analysis Of Urea Ionic Co-Crystals**

The effectiveness of emancipation in water and soil was tested using a slow release analysis. The P-methyl Amino Benzaldehyde technique by using a UV VIS Spectrophotometer, and a Soil Leaching Column were utilized to analyze the release rate and effectiveness of simple and ionic co-crystals urea.

#### **3.5.1 UV VIS Spectrophotometry**

The P-methyl Amino Benzaldehyde methodology was used to examine the release rate and effectiveness [82] of urea and urea ionic co-crystals. Using a GENESYSTM 20 UV-Visible spectrophotometer, the standard curve was first generated using Analytical grade urea prills (extra Pure). The gradient of the drawn calibration curve was calculated using standardized concentrations of analytical grade urea (20ppm, 40ppm, 60ppm, 80ppm, and 1000ppm). The absorbance of these reference solution was measured by a UV-Visible Spectrophotometer, as indicated in Table. 3.2. Afterwards, as illustrated in Figure 3.5-1, a standard curve was produced by drawing a plot between known urea concentration and absorbance. The below is the test methodology for the dissolution rate of combinations.

##### **3.5.1.1 Test Procedure**

In a 2.5 liter glass beaker filled with deionized water, 5 g of sample urea crystals were added. At time internals of 3 minutes, 6 minutes, 9 minutes, 12 minutes, 15 minutes, 30 minutes, 1 hour, and 2 hours, 5 ml of specimen aliquots were collected from the

midst of the glass and diluted to 25 ml for measuring the absorption using a UV-Visible Spectrophotometer methodology. Prior to samples aggregation, the glassware was shaken for 15 seconds. Then 10 ml sample was taken out of a 50 ml jar having diluted sample and put in a 50 ml volumetric flask along with 1 ml Hydrochloric Acid (1:1) and 5 ml p-Dimethyl Amino Benzaldehyde solution, as well as de-ionized water to make it up [83]. Lastly, optical density was measured at a wavelength of 418nm to determine the untold urea crystals concentration, rate of release, and efficiency.

$$\text{Urea(ppm)} = (\text{Absorbance} - \text{Y. Intercept}) \div (\text{Slope from calibration curve}) \dots (1)$$

$$\text{Efficiency (\%)} = C_U - C_{UI} / C_U \times 100 \dots (2)$$

Where,

$C_U$  and  $C_{UI}$  are the concentrations (ppm) in the simple and ionic co-crystals urea samples at 15 min, respectively.

Table 3. 2. Urea Concentration (ppm) Vs. Absorbance (Au).

S.No.	Urea (ppm)	Absorbance (Au)
01	0	0
02	20	0.024
03	40	0.051
04	60	0.072
05	80	0.096
06	100	0.12

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

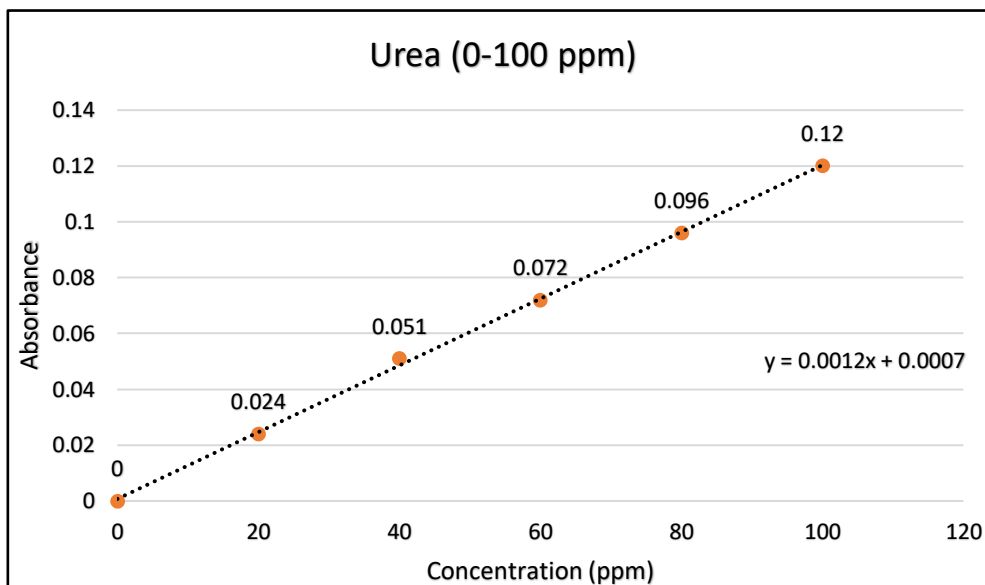


Figure 3.5- 1. Standard Curve Of Urea Concentration And Absorbance. [82]

### 3.6 Pot Test Experimentation

#### 3.6.1 Experiment Location

The glass house in the department of Atta Ur Rahman School of Applied Biosciences, National University of Sciences & Technology (NUST), Islamabad, Pakistan, was opted for field analysis, located at altitude 508 m, latitude and longitude of 33.64636 °N and 72.98788 °E, sequentially, from sea level of reference. The temperature in the location may range from -4 to 25 °C and up to 40 °C, respectively during winter and summer.

#### 3.6.2 Experimental Work Design

The pot plan was accomplished in a totally randomised layout, a total of 5 treatments and 6 replicates were used for the field analysis work. The pot top and bottom diameter were 17 cm and 12 sequentially, while the height and area of the pot were respectively 22 cm and 0.016 m<sup>2</sup>. The soil filled in each pot was 02 kg. N, P, and K were applied at a standard rate of 75 kg/hac, 25 kg/hac, and 50 kg/hac respectively at the planting time. The field analysis work was carried out on Spinach (F1 Hybrid) plants, and two seeds were sown at 9 different places of each pot. Later on, at the time of the seed sprouting trimming was performed to keep 5 plants per pot. Every day, watering of plants was done to ensure a moisture content of 70% per pot, after calculating the water



holding capacity, accordingly. To test the efficacy of ionic co-crystals in real-world situations, field analyses of soil, roots and shoots were conducted and presented.

### **3.6.3 Treatments**

T1: Control

T2: UC Urea

T3: UIC-1 Urea

T4: UIC-2 Urea

T5: UIC-3 Urea

## **3.7 Soil Analysis**

Soil testing was performed at Barrani Agriculture Research Institute (BARI) in Chakwal. Soil was humus type, with pH 7.70, Saturation percentage (SP) 31, ECe 0.58 ds/m, and organic matter 0.52 percent. The amount of macronutrients (K, P, and N) was calculated as 118 mg/kg, 6.5 mg/kg, and 0.026 percent, respectively using Estefan et al. approach's [87]. Various analyses of soil were conducted, including Soil Moisture Content, Water Holding Capacity, pH, Electrical Conductivity (EC), Total Organic Carbon (TOC), Organic Matter, Microbial Biomass Carbon (MBC), Microbial Biomass Nitrogen (MBN), Microbial Biomass Phosphorus (MBP), Microbial Biomass Potassium (MBK), Leaching Test, Mineral Nitrogen Contents i.e. Nitrate-Nitrogen ( $\text{NO}_3^-$ ), Ammonium-Nitrogen ( $\text{NH}_4^+$ ) [60].

### **3.7.1 Soil Moisture Content**

Soil moisture affects crop growth through altering nutrient availability, nutrient conversions, and soil biological activity. As a result, soil moisture is frequently judged throughout most field testing. All lab assessments are performed on an air- or oven-dry basis, thus the actual soil moisture content must be taken into account [86].

Weigh 10 g fresh soil (2-mm) and dry it overnight at 105 °C in an oven (normally for 24 hours). Remove the container from the oven the next day after the soil has dried, cool in a desiccator for at least 30 minutes, and re-weigh. The following formulas will be used for calculating soil moisture content and moisture factor [87].

$$\text{Soil Moisture } (\Theta) = \frac{\text{Wet Soil (g)} - \text{Dry Soil (g)}}{\text{Wet Soil (g)}} \dots\dots\dots (3)$$

$$\text{Moisture Factor} = \frac{\text{Wet Soil (g)}}{\text{Dry Soil (g)}} \text{ or, } \frac{100 + \% \Theta}{100} \dots\dots\dots (4)$$

### 3.7.2 Water Holding Capacity

The water content of soil after excess gravitational water has absorbed and the pace of downhill water flow has significantly reduced is known as the water-holding capacity (WHC) [87].

For determining the water holding capacity of the soil media, 2 pots were taken and 5 holes were made in each of them, and then filed with soil with 2-3 cm empty space above. Then pots were placed in a water tub and water was added up to the level of soil in the pots. All containers were deposited on upturn strainers for 8 hours for water effluent for an equal amount of time. The weight of the containers was computes which is W1. Then soil was extracted from the containers covered in aluminum foil and withered in a drying oven for 4 to 5 hours at 105°C. Soil weight was measured after drying (Wa). Containers were withered at room temperature weight was measured (Wb). We got values for W2 which is W2 = Wa +Wb and water holding capacity was computed as per g formula given below [88]:

$$\text{100% Water Holding Capacity} = \frac{W_1 - W_2}{W_2} \times 100 \dots\dots\dots (5)$$

After obtaining 100 percent field capacity, the field capacity was measured at 65 percent. We increased the water holding capacity of all pots by 65 percent after seeding. The water loss was then monitored on every day. And kept the water loss constant throughout the trial.

### 3.7.3 pH Of Soil

A suspension of water to soil at a ratio of 2: 1 was used to determine the pH of the soil. To obtain this ratio, 20 g of soil and 40 ml of distilled water will be mixed in a glass to create a soil-water suspension. After agitating the solution for 30 minutes at 25 °C, the pH was determined using a pH meter [87].

### 3.7.4 Electrical Conductivity (EC) Of Soil

The same solution used for pH is utilized to measure the electrical conductivity of samples using an EC meter, by normalizing the EC meter with 0.01 N KCl solution [87].

### 3.7.5 Total Organic Content (TOC) Of Soil

Put 0.5 g soil in a 250 ml beaker. 5 ml 1 N Potassium Dichromate solution and 10 mL concentrated H<sub>2</sub>SO<sub>4</sub> were then injected. The soil in the treatment beaker then whirled to adequately mix it, and fumes were emitted. Let, the beaker achieves ambient temperature to eliminate fumes. 100 mL distilled water and 5 mL concentrated orthophosphoric acid will now be introduced to the beaker solution. Then, use a magnetic stirrer to properly mix the solution. Then insert 10-15 drops of diphenylamine indicator and agitate the solution until it turns violet-blue. To titrate the solution, ferrous ammonium sulphate solution (0.5 M) was utilized. The appearance of a bright green colour signifies that the titration is done. For blank sample, with no soil, all reagent will be mixed and titrated ferrous ammonium sulphate solution (0.5 M). The TOC of soil is calculated using the formula below [87].

$$\% \text{ Oxidizable Organic Carbon} = \frac{[V_B - V_S] \times 0.3 \times M}{W_t} \dots\dots (6)$$

$$\% \text{ Total Organic Carbon} = 1.334 \times (\% \text{ Oxidizable Organic Carbon}) \dots\dots (7)$$

$$\% \text{ Organic Matter} = 1.724 \times (\% \text{ Total Organic Carbon}) \dots\dots (8)$$

Where,

M = Molarity of ferrous ammonium sulphate solution (about 0.5 M)

V<sub>B</sub> = Volume of ferrous ammonium sulphate solution required to titrate the blank (ml)

V<sub>S</sub> = Volume of ferrous ammonium sulphate solution required to titrate the sample (ml)

W<sub>t</sub> = Weight of air-dry soil (g)

0.3 =  $3 \times 10^{-3} \times 100$ , where 3 is the equivalent weight of C

### 3.7.6 Microbial Biomass Carbon (MBC)

The microbial biomass carbon in the soil was measured using a fumigation extraction technique. 5 g soil from the specimen was placed in a test tube and placed in a desiccator with chloroform (ethanol-free) for 36 hours. After that, remove the test tubes from the desiccator and place them in the water bath for 120 minutes at 80°C. The soil from the test is then removed to the beaker. Then insert 25 mL of 0.5 M K<sub>2</sub>SO<sub>4</sub> solution and agitate the solution constantly for 2 h in a shaking orbital incubator. The filtration of solution was done using Whatman no. 42 filter paper. Add 5 g soil and mix it with 25 ml of 0.5 M K<sub>2</sub>SO<sub>4</sub> solution for non-fumigated samples. To get the clear filtrate, the solution was well swirled, and Whatman no. 42 filter paper was used.

Take 4 ml extract in a 250 ml beaker to estimate microbial biomass carbon. 5 ml 1 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution and 10 mL concentrated H<sub>2</sub>SO<sub>4</sub> are now included. The soil in the solution flask was whirled to adequately mix it, and fumes were emitted. Let, the beaker achieves ambient temperature to eliminate fumes. 100 ml distilled water and 5 mL concentrated orthophosphoric acid will now be injected to the beaker solution. Then, use a magnetic stirrer to properly mix the solution. Then insert 10-15 drops of diphenylamine indicator and agitate the solution until it turns violet-blue. To titrate the solution, ferrous ammonium sulphate solution (0.5 M) was utilized. The appearance of a bright green colour signifies that the titration is done. For blank sample, with no soil, all reagent will be mixed and titrated ferrous ammonium sulphate solution (0.5 M). The MBC of soil is calculated using the formula below [89-90].

$$\text{Biomass-Carbon} = (B - V) \times N \times 0.003 \times \frac{100 + \theta}{w_t} \times \frac{1000}{v_1} \times 1000 \dots (9)$$

$$\text{Microbial Biomass-Carbon (ppm)} = (C_{\text{fumigated}} - C_{\text{control}}) \dots (10)$$

Where:

V = Volume of 0.2 N [ferrous ammonium sulphate solution] titrated for the sample (ml)

B = Digested blank titration volume (ml)

N = Normality of [ferrous ammonium sulphate solution] solution

$W_t$  = Weight of oven-dry soil (g)

$V_1$  = Volume of soil digest used for measurement (ml)

$\theta$  = Weight of water per oven-dry soil (g)

$0.003 = 3 \times 10^{-3}$ , where 3 is equivalent weight of C

### 3.7.7 Microbial Biomass Nitrogen (MBN)

The same strategy described above for Microbial biomass carbon will be used for Microbial biomass nitrogen and is regulated by using the Kjeldahl apparatus. The following formula is used to determine MBN [87, 89-90].

$$\text{Biomass-N (ppm)} = (V - B) \times N \times 14.01 \times \frac{100 + \theta}{W_t} \times \frac{250}{V_1} \times \frac{1000}{V_2} \times 1000$$

..... (11)

$$\text{Microbial Biomass-Nitrogen (ppm)} = (N_{\text{fumigated}} - N_{\text{control}}) \dots (12)$$

Where,

$V$  = Volume of 0.01 N  $H_2SO_4$  titrated for the sample (ml)

$W_t$  = Weight of oven-dry soil (g)

$B$  = Digested blank titration volume (ml)

$N$  = Normality of  $H_2SO_4$  solution

$V_1$  = Volume of soil extract used for digestion (ml)

$V_2$  = Volume of soil digest used for distillation (ml)

14.01 = Atomic weight of N

$\theta$  = Weight of water (g) per oven-dry soil

### 3.7.8 Microbial Biomass Phosphorus (MBP)

By making use of a fumigation extraction technique the microbial biomass phosphorus in soil was regulated [91, 92]. 5 g soil from the specimen was transferred in a test tube and placed in a desiccator with chloroform (ethanol-free) for 36 hours. After that, remove the test tubes from the desiccator and place them in the water bath for 120 minutes at 80°C. The soil from the test is then removed to the beaker. Then insert 25 ml of 0.5 M NaHCO<sub>3</sub> solution [93] and agitate the solution constantly for 2 h in a wobbling round inoculator . The filtration of solution was done using Whatman no. 42 filter paper. Add 5 g soil and mix it with 25 ml of 0.5 M NaHCO<sub>3</sub> solution for non-fumigated samples. To get the clear filtrate, the solution was well swirled, and Whatman no. 42 filter paper was used.

To measure the MBP, add 1 ml of extract in a test tube and add 2.5 mL of colour developing solution. The optical density of phosphorus was measured using a spectrophotometer (Cecil, CE2021, 2000 configuration) [87, 94-96].

Table 3. 3. MPB Concentration (mg/kg) Vs. Absorbance (Au).

S.No.	Concentration (mg/kg)	Absorbance (Au)
01	0	0
02	3.94	0.216
03	7.87	0.38
04	11.81	0.55
05	15.75	0.74
06	19.69	0.99
07	23.62	1.23

Absorptivity or “a” or Slope of the curve = 0.0508.

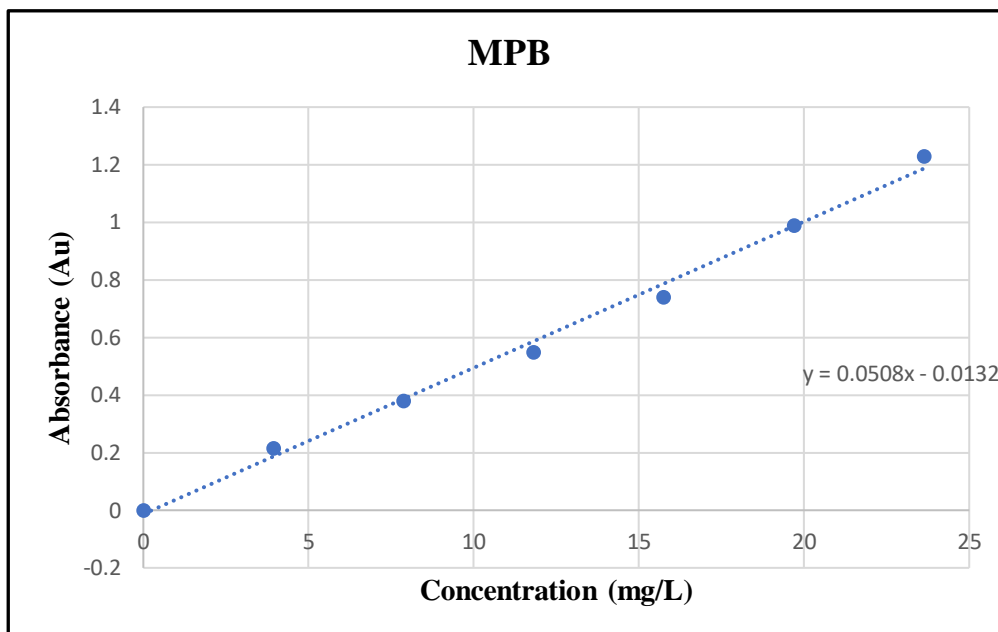


Figure 3.7- 1. Standard Curve Of MBP Concentration And Absorbance.

### 3.7.9 Microbial Biomass Potassium (MBK)

The microbial biomass potassium in soil was determined using a fumigation extraction technique [91, 92]. 5 g soil from the specimen was transferred in a test tube and placed in a desiccator with chloroform (ethanol-free) for 36 hours. After that, remove the test tubes from the desiccator and place them in the water bath for 120 minutes at 80°C. The soil from the test is then removed to the beaker. Then insert 25 ml of 0.5 M  $C_2H_7NO_2$  solution [97] and agitate the solution constantly for 2 h in a wobbling round inoculator. The filtration of solution was done with the help of Whatman no. 42 filter paper. Add 5 g soil and mix it with 25 ml of 0.5 M  $C_2H_7NO_2$  solution for non-fumigated samples. To get the clear filtrate, the solution was well swirled, and Whatman no. 42 filter paper was used.

To measure the MBK, add 5 ml of extract in test tube and (Jenway, PFP7) flame photometer used to determine the potassium content [98, 99].

Table 3. 4. MPK Concentration (ppm) Vs. Absorbance (Au).

S.No.	Concentration (ppm)	Absorbance (Au)
01	0	0
02	0.5	0.09
03	1	0.2
04	1.5	0.24
05	2	0.35
06	2.5	0.4
07	3	0.46

Absorptivity or “a” or Slope of the curve = 0.1536.

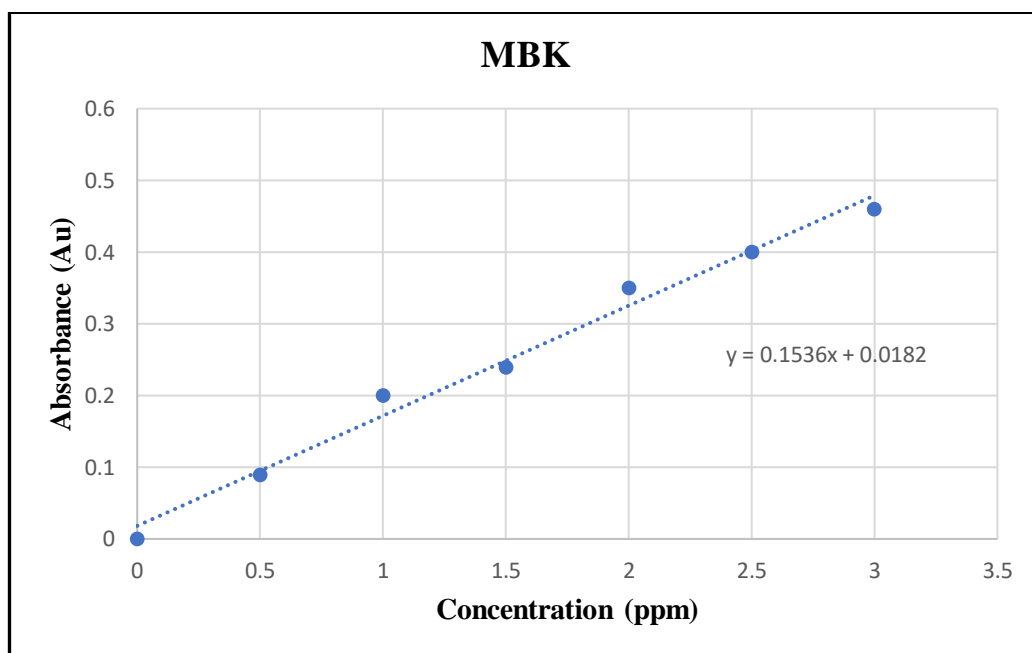


Figure 3.7- 2. Standard Curve Of MBK Concentration And Absorbance.

### 3.7.10 Mineral Nitrogen Contents In Soil And Leachate

Mineral nitrogen content in soil and leachate is quantified using a standardized 96-well microplate configuration and microplate reader, which simplifies quantitation of any of the nutrients much easier [100]. Similar reagents as the standard procedures, [101, 102] were adopted to develop the colour for nitrate and ammonium estimation.



### 3.7.10.1 Nitrate Nitrogen ( $\text{NO}_3^- - \text{N}$ )

A suite of microplate reader-based colorimetric methods [100] was used to determine the nitrate-nitrogen [101] contents in soil and leachate, the standard curve was first generated by dissolving 7.218 g dry potassium nitrate in 600 ml distilled water and dilution was done to 1000 ml. Then pipette 0, 0.20, 0.40, 0.60, 1.00, and 1.20 ml of the stock standard solution into 100 ml volumetric flask and make the volume with 1M KCl. The resulting standard concentrations are 0, 2, 4, 6, 10, and 12 mg  $\text{NO}_3^- - \text{N}$   $\text{L}^{-1}$ . Now absorbance was noted using a microplate reader, as indicated in Table. 3.5. Afterwards, as illustrated in Figure. 3.7-3., a standard curve was produced by drawing a plot between known nitrate concentrations and absorbance. The test procedure is given below.

#### 3.7.10.1.1 Test Procedure

First of all extraction solution of 0.5M  $\text{K}_2\text{SO}_4$  was prepared. 5 g of soil or 5 ml of leachate from specimen along with 10 ml extraction solution was taken and shaking was done continuously for 30 min at 60 rpm. Then filtration of sample was done using a Whatman no. 42 filter paper. Then similar reagents as the standard procedures, [101] were adopted to develop the colour which includes [100]:

- i. Vanadium Chloride ( $\text{VCl}_3$ ) i.e. (0.8 g of  $\text{VCl}_3$  in 50 ml of concentrated HCl).
- ii. 2.0% Sulfanilamide solution i.e. (2 g Sulfanilamide bring to 100 ml volume with 5% (v/v) HCl).
- iii. 0.1% (w/v) NEDD (N-(1-naphthyl) ethylenediamine dihydrochloride) i.e. (100 mg NEDD dissolve in water and bring volume up to 100 ml).

After that combine solutions before analysis to a ratio of 2:1:1 (20 ml  $\text{VCl}_3$  : 10 ml Sulfanilamide : 10 ml NEDD). After that 100  $\mu\text{l}$  of premix solution was added to 100  $\mu\text{l}$  of each sample solution in a 96 well plate. The plate is inoculated for 1 hr at 37°C. and absorbance was noted at 540 nm with the help of a microplate reader to determine the unknown nitrate concentration [100].

$$\text{Nitrate-Nitrogen (mgL}^{-1}\text{)} = (\text{Absorbance} - \text{Y. Intercept}) \div (\text{Slope from calibration curve}) \dots\dots\dots (13)$$

Table 3. 5. ( $\text{NO}_3^- - \text{N}$ ) Concentration (mg/L) Vs. Absorbance (Au). [100, 101]

S.No.	Concentration (mg/kg)	Absorbance (Au)
01	0	0.366
02	1.91	0.549
03	3.81	0.700
04	5.71	0.864
05	7.62	1.029
06	9.52	1.22
07	11.43	1.343

Absorptivity or “a” or Slope of the curve = 0.0863.

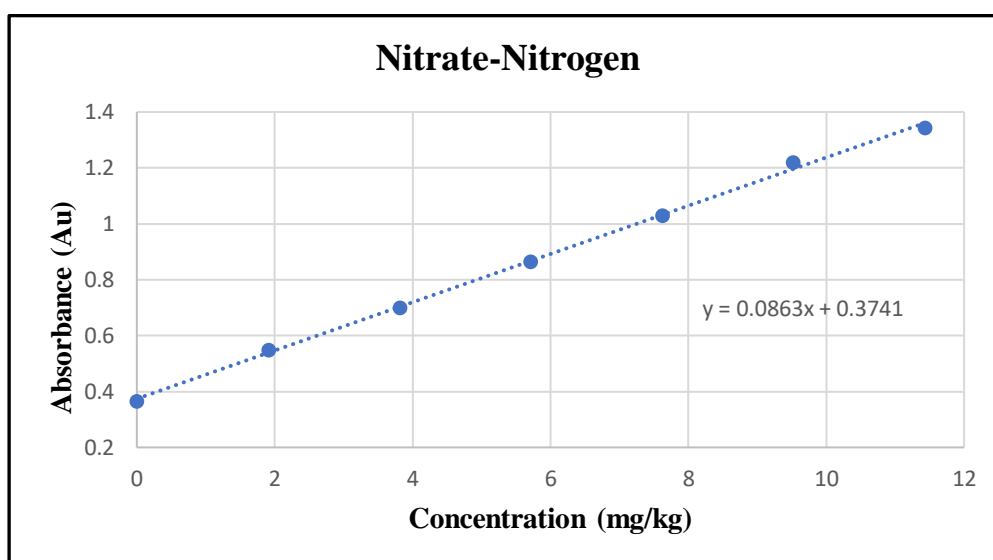


Figure 3.7- 3. Standard Curve Of Nitrate-N Concentration & Absorbance. [100, 101]

### 3.7.10.2 Ammonium-Nitrogen ( $\text{NH}_4^+ - \text{N}$ )

A suite of microplate reader-based colorimetric methods [100] was used to determine the ammonium-nitrogen [102] contents in soil and leachate, the standard curve was first generated by dissolving 4.719 g dry ammonium sulfate in 400 ml distilled water and dilution was done to 1000 ml. Then pipette 0, 0.5, 1.0, 1.5, 2.0, and 2.5 ml of the stock standard solution into 100 ml volumetric flask and make the volume with 1M KCl. The resulting standard concentrations are 0, 5, 10, 15, 20, and 25 mg  $\text{NH}_4^+ - \text{N}$   $\text{L}^{-1}$ . Now absorbance was noted using a microplate reader, as indicated in Table. 3.6. Afterwards, as illustrated in Figure. 3.7-4., a standard curve was produced by drawing

a plot between known ammonium concentrations and absorbance. The test procedure is given below.

### 3.7.10.2.1 Test Procedure

First of all extraction solution of 2M KCl was prepared. 5 g of soil or 5 ml of leachate from specimen along with 50 ml extraction solution was taken and shaking was done continuously for 60 min at 60 rpm. Then filtration of sample was done using a Whatman no. 42 filter paper. Then similar reagents as the standard procedures, [102] were adopted to develop the colour which includes [100]:

- i. 16.3 mM Trisodium Citrate Dihydrate.
- ii. 4 mM Phenol and 13.4 mM Sodium Nitroprusside.
- iii. 2 ml Sodium Hypochlorite solution with 98 ml 0.5M Sodium Hydroxide solution.

After that add 200 µl of sample solution followed by each 10 ml all colour developing reagents in a microplate. The plate is then vortexed at 750 rpm for 2 min on the microplate catalyst between inclusion of each reactant. Then cover the microplate with an optically vivid adhesive microseal (BioRad #MSB1001) to circumvent any taint and vulnerability to vapors of phenol. Then placed it in the dark during 2 hr. reaction time and optical density was noted at 630 nm to find the unknown ammonium concentration [100].

$$\text{Ammonium-Nitrogen (mgL}^{-1}\text{)} = (\text{Absorbance} - \text{Y. Intercept}) \div (\text{Slope from calibration curve}) \dots\dots\dots (14)$$

Table 3. 6. (NH<sub>4</sub><sup>+</sup> – N) Concentration (mg/L) Vs. Absorbance (Au). [100, 102]

S.No.	Concentration (mg/kg)	Absorbance (Au)
01	0	0.0358
02	4.76	0.0377
03	9.52	0.0409
04	14.29	0.046
05	19.05	0.0493
06	23.81	0.0525

Absorptivity or “a” or Slope of the curve = 0.0007.

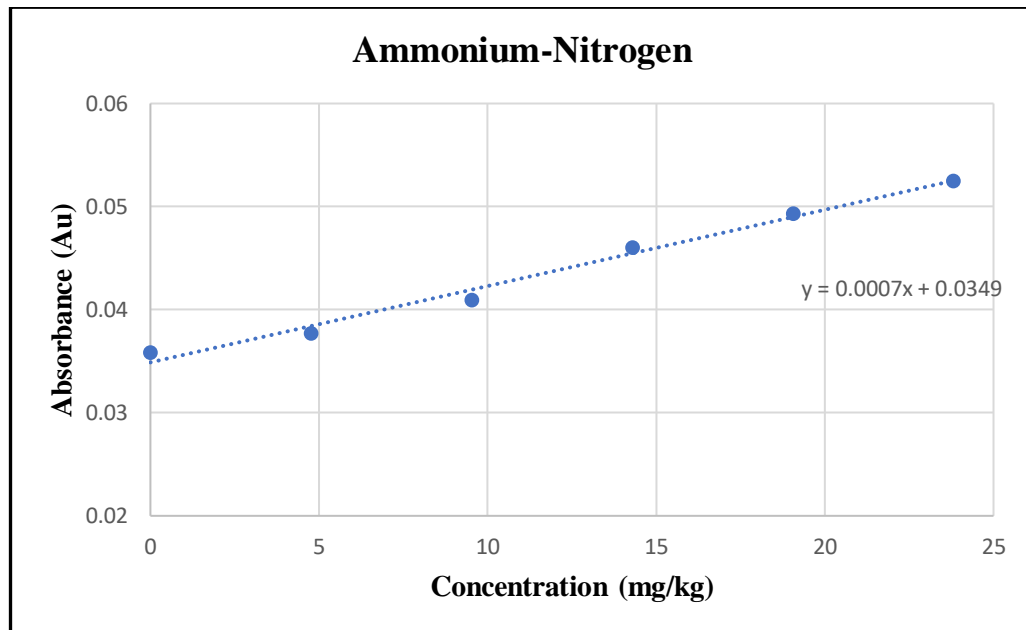


Figure 3.7- 4. Standard Curve Of Ammonium-N Concentration & Absorbance. [100, 102]

### 3.8 Plants Analysis

The spinach plants were harvested twice i.e. after 35 days and 65 days. Leaves were collected after both harvesting and fresh weight was calculated immediately, afterwards leaves were scrubbed with deionized water and withered in oven for 48 hours at 70°C and dry weight was calculated as well. Furthermore, one day prior to harvesting chlorophyll values of every pot plants were calculated with the help of SPAD meter, along with that plants diameter, height, and leaf area was also noted. Chlorophyll values (a, b, and carotenoids) were also calculated with the help of UV VIS Spectrophotometer at their respective wavelengths.

After the final harvesting, roots and shoots were separated for further analysis. Roots were detached from the earth with the aid of a tool, and the dirt on the roots was entirely removed. The roots were then placed water bath for 120 minutes. The soil bunch around the roots breaks after the water dousing, and roots were separated completely, and the fresh weight of roots was noted. Then roots were dried in oven, and dry weight was also noted. Soil samples were also taken from each pot and fresh and dry weight was calculated and kept for further analysis. The parameters that will be estimated after the crop has been harvested are given as follow:

- Plant Height
- Plant Diameter

- Leaf Area
- Fresh Weight (shoots, roots)
- Dry Weight (shoots, roots)
- Chlorophyll Values Via SPAD Meter
- Chlorophyll Values a, b, and carotenoids
- Plant Nitrogen Uptake
- Apparent Nitrogen Recovery

### **3.8.1 Plant Height**

The height of the spinach plants was measured after it was chopped. Three specimens were chosen from each pot for this task, and their height was estimated in centimeters with a measuring rod.

### **3.8.2 Plant Diameter**

The diameter of the spinach plants was measured after it was chopped. Three specimens were chosen from each pot for this task, and their diameter was estimated in millimeters with a vernier, and then converted in centimeters.

### **3.8.3 Leaf Area**

Three leaves out of each plant were chosen and detached from the plant for the sake of calculating leaf area. Then, a leaf area meter will be used to calculate the amount of leaf area per pot in  $\text{cm}^2$ .

### **3.8.4 Fresh Weight**

Fresh weight was calculated as soon as the crop is harvested. Plants are chopped into tiny parts for this task and then weight in grams is now measured using a weight balance. Also the fresh weight of roots and soil is calculated after the final harvesting.

### **3.8.5 Dry Weight**

Fresh specimen are withered at  $70^\circ\text{C}$  for 48 hours to regulate the dry weight. Plant dry weight in grams is now determined using a weight balance [103]. Also the dry weight of roots and soil is calculated after the final harvesting.

### 3.8.6 Chlorophyll Values

The chlorophyll contents of plants were measured using two different methods, as given below:

#### 3.8.6.1 Chlorophyll Values Via SPAD Meter

For measuring chlorophyll content, we used the SPAD-502Plus chlorophyll meter. For each plant in a healthy condition, three values were taken and then an average was calculated.

#### 3.8.6.2 Chlorophyll Values a, b, And Total Chlorophyll

For measuring chlorophyll contents a, b, and, total chlorophyll, Arnon (1949) gave the equation for extraction with ethanol and acetone and absorbances at 645 nm and 663 nm as shown below. A tiny part of leaf from each pot is taken and put in a solution containing Ethanol, Acetone, and Distilled Water (45:45:10), and kept in a dark until solution absorbed all contents from leaf. Then absorbance will be measured for chlorophyll a, b, and carotenoids at a wavelength of 663 nm, 645 nm, and 473 nm respectively, by using UV VIS Spectrophotometer. Then chlorophyll values will be measured using following formulas:

$$\text{Chl (a)} = 12.71 \times (\text{A663}) - 2.69 \times (\text{A645}) \dots\dots (15)$$

$$\text{Chl (b)} = 22.9 \times (\text{A645}) - 4.68 \times (\text{A663}) \dots\dots (16)$$

$$\text{Total Chlorophyll} = 20.02 (\text{A645}) + 8.02 (\text{A663}) \dots\dots (17)$$

### 3.8.7 Apparent Nitrogen Recovery

The nitrogen content of the plant is measured using the Kjeldahl equipment. Fill the digestion tube with 5 g of crushed dry plant powder. After that, add 3.5 g digestive catalyst mixture and 10 ml concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and whirl properly. Heat at 420 °C for at least 3 hours. The second process is distillation, which involves distilling ammonia with a 40 percent sodium hydroxide (NaOH) solution and trapping and forming solvated ammonium ions with boric acid (H<sub>3</sub>BO<sub>3</sub>). The titration is now carried out using 0.01N H<sub>2</sub>SO<sub>4</sub> [87]. The ANR (%) of the plant is calculated using the formula below:

$$\text{Nitrogen Apparent Recovery (\%)} = \frac{(N_s \times \text{DM}_s) - (N_o \times \text{DM}_o)}{\text{TN}_\alpha} \text{ [104] } \dots\dots (18)$$

Where,

$N_s$  = N content in spinach plant sample [kg N]

$DM_s$  = Spinach DM yield (kg/hac)

$N_o$  = Spinach N content in control treatment

$TN_\alpha$  = Total amount of applied N (kg/hac) by NPK in the pots

### **3.9 Statistical Analysis**

Statistical analysis was done by analysis of discrepancy using data 8.1. For each variable the consequence of treatments were examined, among the treatments further comparison was made among prominent variations that were additionally collated using LSD test at a 5 % probability level [72, 86].

# Chapter 4

## Results and Discussions

Results from applied characterization approaches that were thoroughly investigated and assessed are presented in this chapter.

### 4.1 Release Rate Analysis Of Urea Ionic Co-Crystals

#### 4.1.1 UV VIS Spectrophotometry

The objective of this experimental procedure was to determine at what rate urea was released after it was applied to urea prills. To examine the delayed release of treated urea, UV-Spectroscopy was used. The experiment was conducted after the ionic co-crystals urea were put in the de-ionized water. Untreated prills also were examined for correlation. This experiment also determines how effective ionic co-crystals are at limiting urea release. To conduct the release test, all urea crystal variants were tested, and the findings were presented with reference to urea concentration in ppm using equation (A). The effectiveness of each combo was determined by examining the urea concentration in untreated and treated samples at 15 minutes using formula (B). The concentrations of untreated and treated urea prills at various time intervals can be seen in Table. 4.1.

Table 4. 1. Concentration Of Untreated Urea and Urea Ionic Co-Crystals. [82]

S. No.	Time (min)	Urea (ppm)	UIC-1 (ppm)	UIC-2 (ppm)	UIC-3 (ppm)
01	3	34.25	25.75	28.92	26.92
02	6	40.25	29.92	29.58	30.5
03	9	45.08	31.25	30.25	31.42
04	12	47.58	34.08	31.75	32.9
05	15	61.08	36.1	36.58	33.42
06	30	80.4	39.25	39.92	36.4
07	60	80.4	43.58	49.8	38.08
08	120	80.4	49.6	59.9	46.75



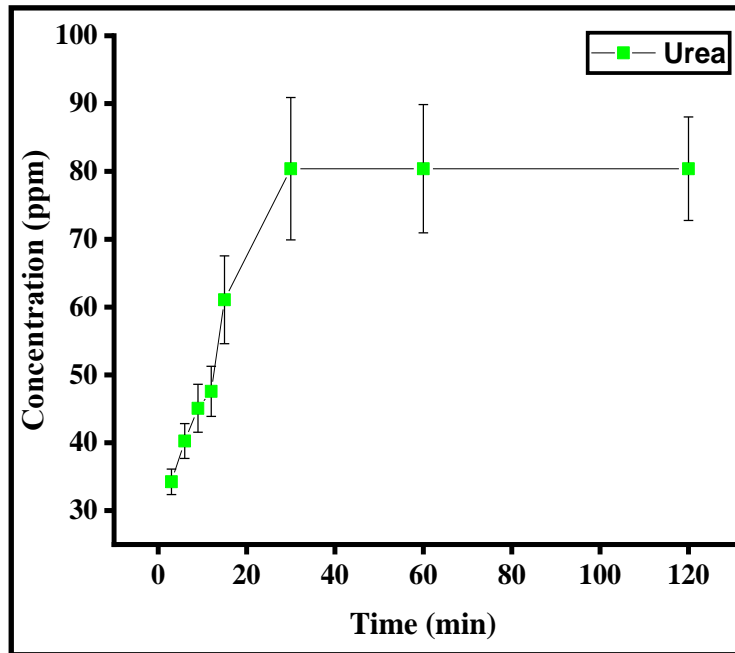


Figure 4.1- 1. Untreated Urea Release: Time (min) Vs. Urea Concentration (ppm).

The correlation between untreated urea concentrations (ppm) and time (min) is depicted in Figure. 4.1-1. The concentrations of urea were determined by equation (A), that stated that absorbance directly proportionate to concentration. Urea concentrations rise with increasing absorbance values. The untreated urea, promptly dissolve in water and is no longer visible to the human eye. Because there is no compaction with C-0, so it will follow the burst release mechanism. It occurred as a result of the revealed surface layer, that allows water molecules to penetrate more readily.

Based on the composition of the compacting material employed, all materials compacted with urea tend to reduce speed nutrient discharge to a certain level. In comparison to untreated urea, urea ionic co-crystals dissipated gently at first. It was caused by the application of compaction, that inhibits urea ejection from the substrate towards the bulk solution. The compacting material in UIC-1 progresses the slow release and reduce the release rate up to 2.01 times, as depicted in Figure. 4.1-2.

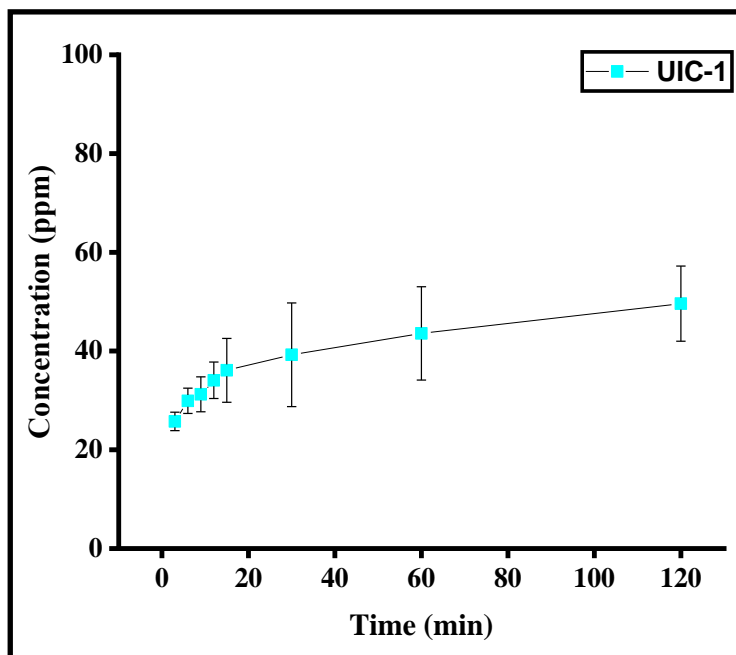


Figure 4.1- 2. UIC-1 Urea Release: Time (min) Vs. Urea Concentration (ppm).

Figure. 4.1-3. described the release of UIC-2 urea, in which urea nitrate was used as a compacting material along with other salts used in UIC-1. UIC-2 urea fertilizer progresses the slow release and reduce the release rate up to 1.67 times.

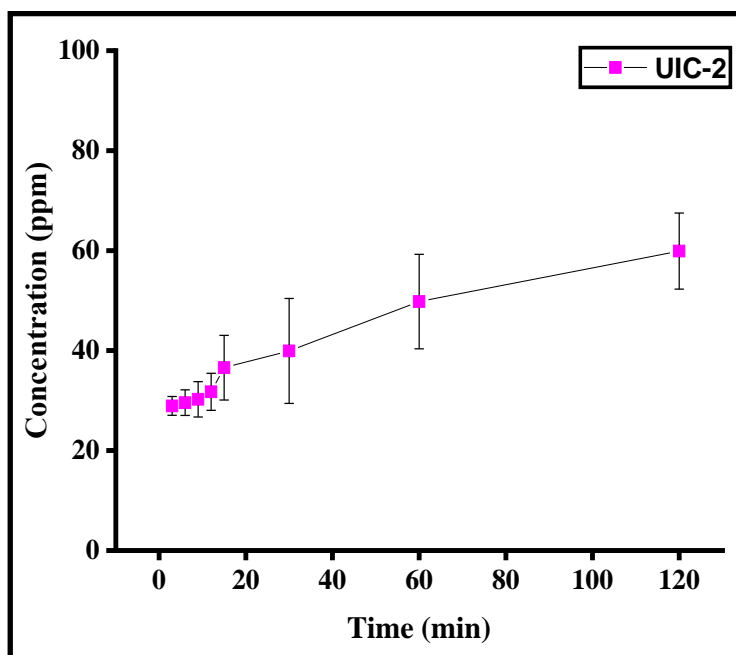


Figure 4.1- 3. UIC-2 Urea Release: Time (min) Vs. Urea Concentration (ppm).

In contrast, as depicted in Figure. 4.1-4. which depicts the release of UIC-3 urea, in which urea phosphate was used instead of urea nitrate along with other compacted materials used in UIC-1. UIC-3 urea fertilizer progresses the best result for slow release and reduce the release rate up to 2.13 times.

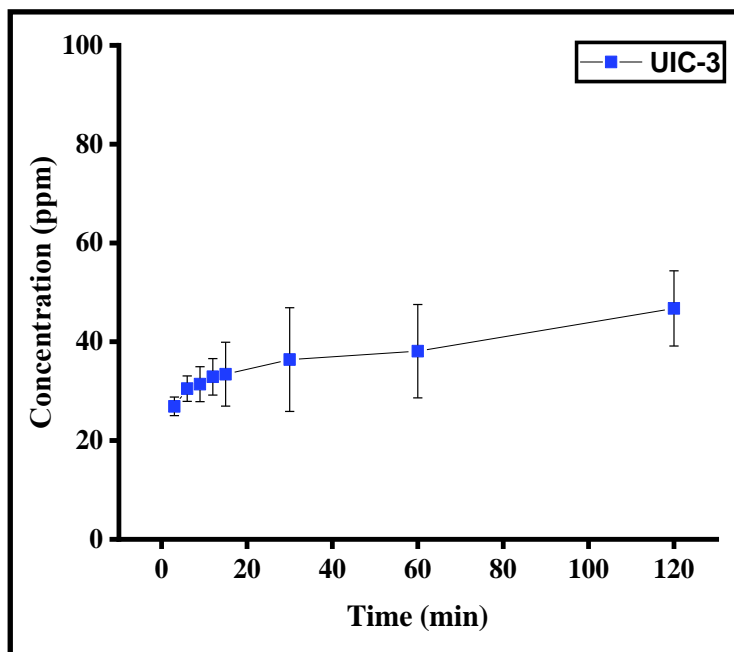


Figure 4.1- 4. C-3 Urea Release: Time (min) Vs Urea Concentration (ppm).

Table. 4.2 and Figure. 4.1-5. depicted the efficiency of urea ionic co-crystals which was calculated using the efficiency equation (B). UIC's and uncompacted urea concentrations were used at 15 minutes to estimate the efficiency of UIC's.

Table 4. 2. Urea Ionic Co-Crystals Efficiency At 15 Minutes.

Samples	Efficiency (%) At 15 Minutes
UIC – 1	40.90
UIC – 2	40.11
UIC – 3	45.29

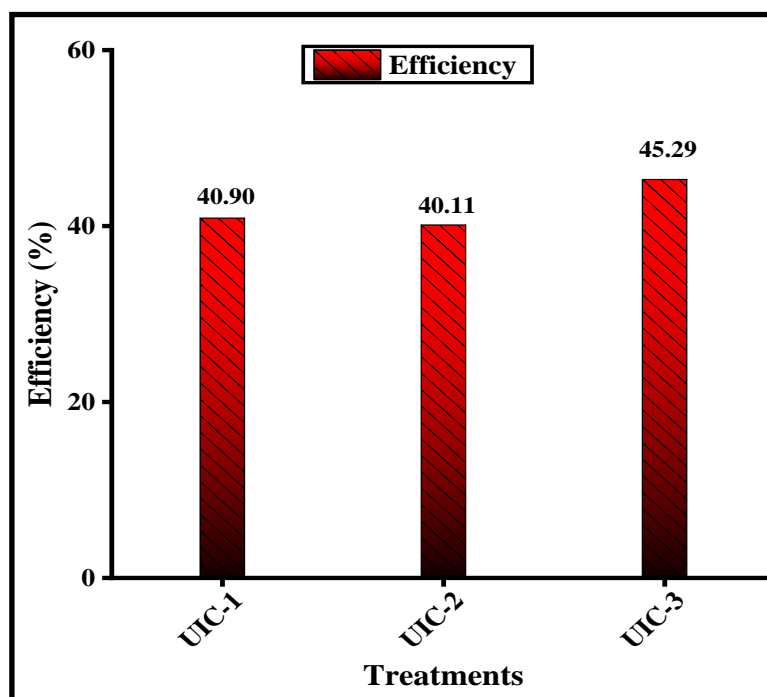


Figure 4.1- 5. UIC's Efficiency At 15 Minutes: Samples Vs. Efficiency (%).

## 4.2 Characterization Of Urea Ionic Co-Crystals

This section covers all of the characterization techniques performed to verify the urea ionic co-crystals. It includes:

### 4.2.1 Scanning Electron Microscope (SEM)

Scanning electron microscopy was used to investigate the surface structure of the simple and urea ionic co-crystals [105]. The crystals surfaces were inspected for porosity, as well as the structure and formulation of the urea's crystals outer structure. A dispersive energy approach was used to assess the elemental composition. The elemental composition of the components was confirmed by EDX analysis.

Figure 4.2-1. depicts SEM micrograph of simple urea (without any application) SEM images at x100 and x3000. The amplification exposes a rugged surface with several patches. The surface is non-uniform, with elevated areas and borders on a few sides.

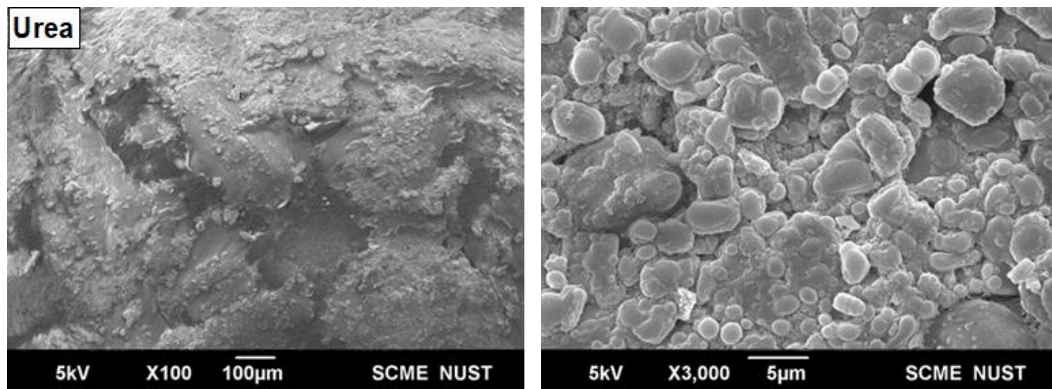


Figure 4.2- 1. SEM Micrograph of Untreated Urea.

Figure 4.2-2. depicts SEM micrograph of UIC-1 treatment having KCl and ZnCl<sub>2</sub> compacted with urea images at x70 and x1000. Combination of KCl and ZnCl<sub>2</sub> with urea with different crystal faces. We observe that the presence of chloride ions at the surface. It is evident from the conclusions that the face is equilibrated in urea solutions and the development of octahedral over cubic crystals is stimulated. The procedure is completely extensive and a diversity of of interfacial characteristics can be understood by its application.

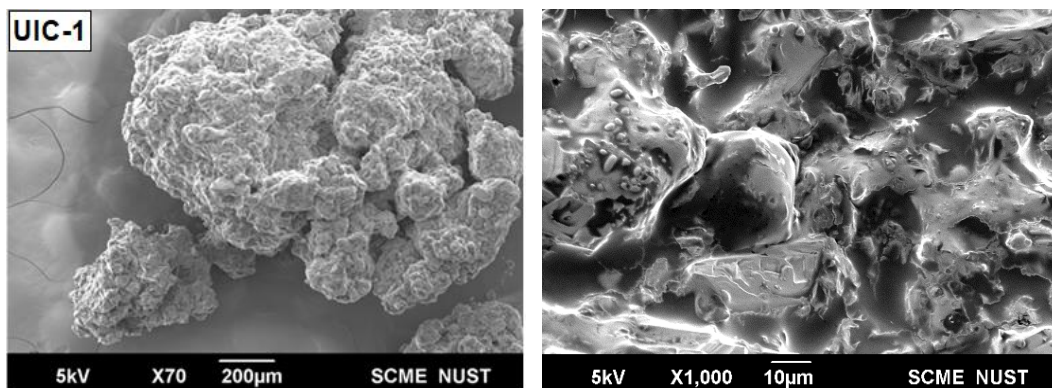


Figure 4.2- 2. SEM Micrograph of UIC-1 Treatment.

Figure 4.2-3. depicts SEM micrograph of UIC-2 treatment having KCl and ZnCl<sub>2</sub> compacted with urea along with Urea Nitrate images at x70 and x3000. The SEM of UIC-3, shows a spongy structure with small pores all over the surface. The whole surface is lumpy. The enlarged image gives an appearance a spongy structure with cluster on someplace because of the union of two film-forming substances.

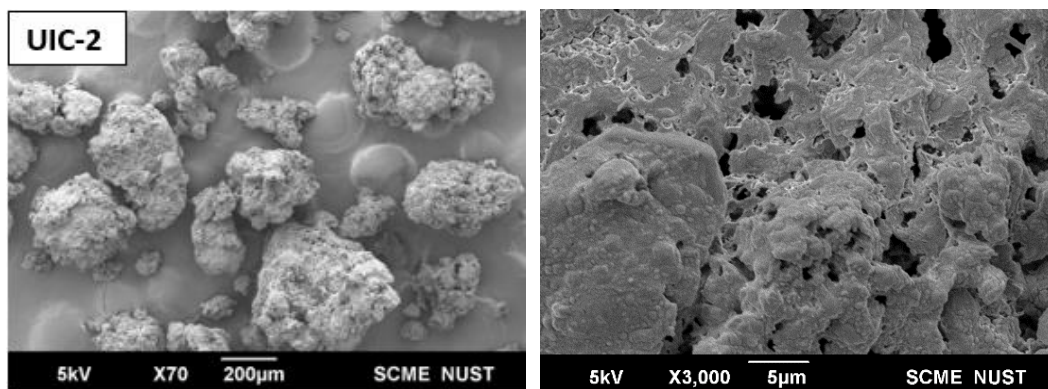


Figure 4.2- 3. SEM Micrograph of UIC-2 Treatment.

Figure 4.2-4. depicts SEM micrograph of UIC-3 treatment having KCl and ZnCl<sub>2</sub> compacted with urea along with Urea Phosphate images at x70 and x3000. The lattice deformation of the crystal came about due to inclusion of KCL. The structure of UIC-3 were specified with the help of a microscope. The crystal configurations were well ordered crystal structures, but the crystal structure of was indeterminate, and a decrease occurs in the aspect ratio of the crystals , which was compatible with the results of XRD.

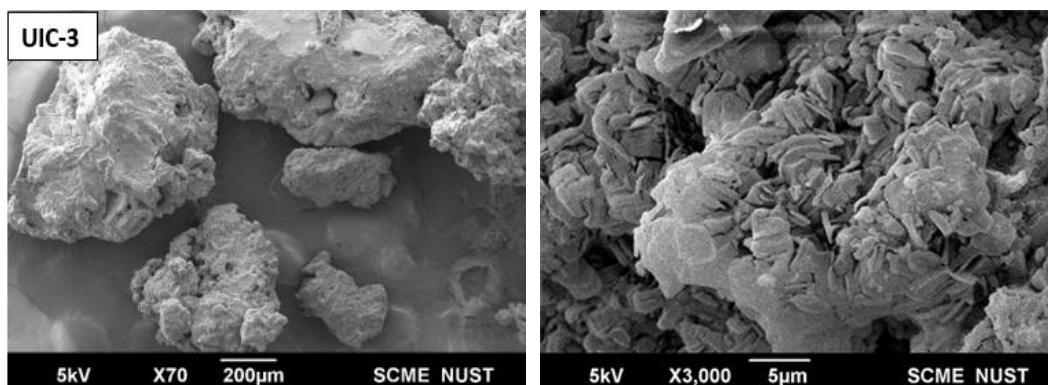


Figure 4.2- 4. SEM Micrograph of UIC-3 Treatment.

#### 4.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR Spectrum of untreated urea and all treatments were done to test the difference in peaks to observe the presence of water and compacted materials. The FTIR spectrum of untreated urea was given in the Figure. 4.2-5. At wavelength 3440 and 3344 cm<sup>-1</sup>, uncoated urea shows asymmetric and symmetric vibrations of NH<sub>2</sub>. At wavelength 2925 cm<sup>-1</sup>, stretching vibrations are exhibited by urea due to the presence of CH and N-H appearances. The peaks in between 2100 cm<sup>-1</sup> and 2500 cm<sup>-1</sup> show the stretching vibrations due to C=O. At peak 2011 cm<sup>-1</sup> bending vibrations are shown by

urea which are attributed to the presence of C and H. At peak  $1625\text{ cm}^{-1}$  is a carbonyl (CO) and at the peak of  $1455\text{ cm}^{-1}$  is a bending vibration NH and CH stretching vibration of  $\text{O} = \text{C-NH}_2$ . Also, the band which appeared at  $1455\text{ cm}^{-1}$  is attributed to  $-\text{CN}$  stretching [106-108]. At  $1159\text{ cm}^{-1}$ , a stretching vibration mode resultant from the  $-\text{C-O-C}$  group can be seen. C-H overtone stretching vibrations are observed at  $1159\text{ cm}^{-1}$ . The peak at  $586\text{ cm}^{-1}$  representing the strong stretching vibrations in urea is imputed to the presence of C & H.

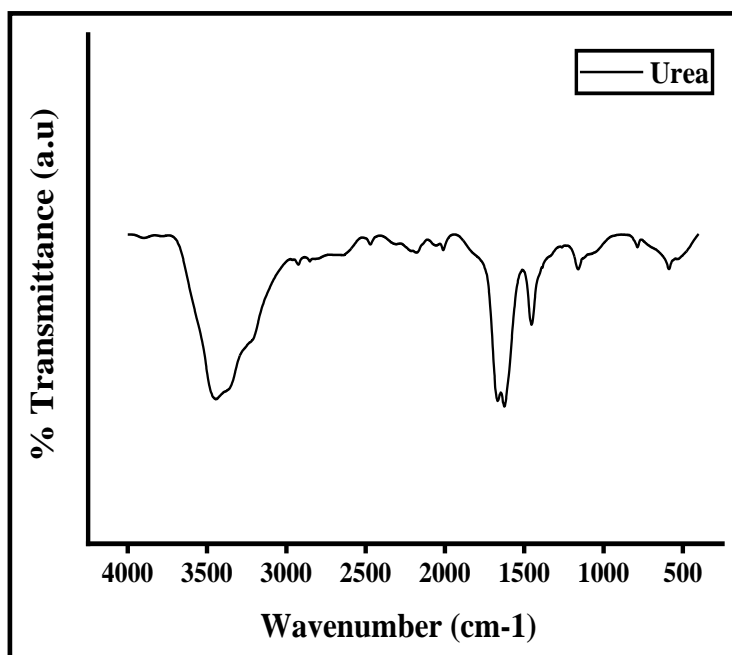


Figure 4.2- 5. FTIR Spectrum Of Untreated Urea.

The FTIR spectrum of UIC-1 was given in the Figure 4.2-6. At wavelength  $3458\text{ cm}^{-1}$  and  $3348\text{ cm}^{-1}$  UIC-1 shows stretching vibration of N-H and O-H like untreated one. At peak  $3256\text{ cm}^{-1}$ , the sample shows an OH vibration, which implied water that is absorbed. At peak  $2220\text{ cm}^{-1}$  is a Nitrile ( $\text{C}\equiv\text{N}$ ) stretching vibration & peak  $2010\text{ cm}^{-1}$  is an Alkyne ( $\text{C}\equiv\text{C}$ ) stretching vibration. At peak  $1622\text{ cm}^{-1}$  is a stretching vibrations of urea due to carbon atom and keto ( $\text{C}=\text{O}$ ) group and at the peak of  $1454\text{ cm}^{-1}$  is a bending vibration NH & stretching CH stretching vibration of  $\text{O} = \text{C-NH}_2$ . At peak  $1330\text{ cm}^{-1}$  strong vibrations are shown by urea corresponding to the presence of C-N linkage. Also, the band which appeared at  $1454\text{ cm}^{-1}$  is attributed to  $-\text{CN}$  stretching. At  $1158\text{ cm}^{-1}$  and  $1263\text{ cm}^{-1}$ , a stretching vibration mode resultant from the  $-\text{C-O-C}$  group can be seen like in untreated urea prill. C-H overtone stretching vibrations are

observed at  $1158\text{ cm}^{-1}$ . The peaks from  $529\text{ cm}^{-1}$  to  $780\text{ cm}^{-1}$  shows the C-Cl stretching of halo compounds.

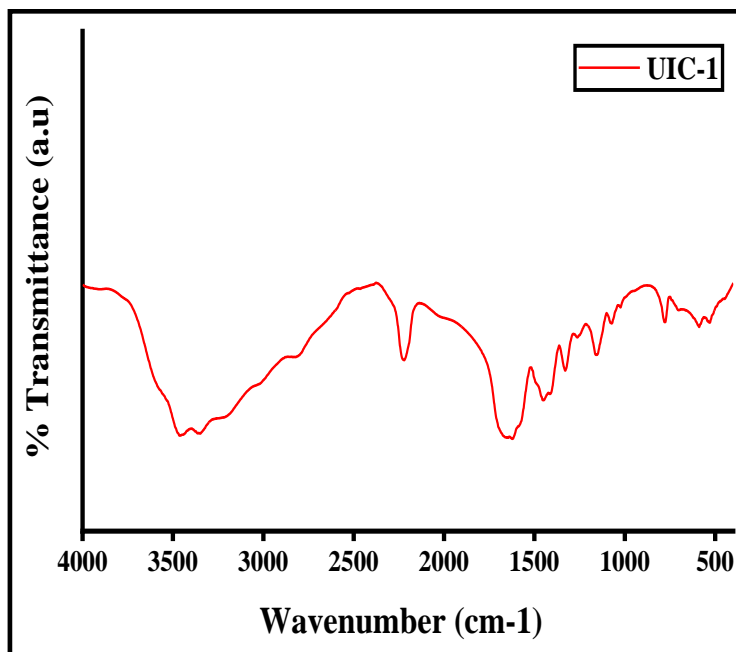


Figure 4.2- 6. FTIR Spectrum Of UIC-1.

The FTIR spectrum of UIC-2 was given in Figure. 4.2-7. At wavelength  $3450\text{ cm}^{-1}$  and  $3357\text{ cm}^{-1}$  UIC-2 shows N-H and O-H stretching vibration like untreated one. At peak  $3256\text{ cm}^{-1}$ , the sample shows an O-H vibration, which implied water that is absorbed. At peaks  $2422\text{ cm}^{-1}$  and  $2216\text{ cm}^{-1}$ , urea shows stretching vibrations due to C-N linkage. The peak at  $2009\text{ cm}^{-1}$  is an Alkyne ( $\text{C}\equiv\text{C}$ ) stretching vibration. At peak  $1622\text{ cm}^{-1}$  is a Carbonyl ( $\text{C}=\text{O}$ ) stretching mode of carbon atom and keto ( $\text{C}=\text{O}$ ) group. The peak  $1652\text{ cm}^{-1}$ , showing bending vibrations of urea is attributed to the presence of amine (N-H). The peak of  $1449\text{ cm}^{-1}$  is a bending vibration NH and CH stretching vibration of  $\text{O}=\text{C}-\text{NH}_2$ . Also, the band which appeared at  $1449\text{ cm}^{-1}$  is attributed to  $-\text{CN}$  stretching. At  $1156\text{ cm}^{-1}$ , a stretching vibration mode resultant from the  $-\text{C}-\text{O}-\text{C}$  group can be seen like in untreated urea prill. C-H overtone stretching vibrations are observed at  $1156\text{ cm}^{-1}$ . The peaks from  $531\text{ cm}^{-1}$  to  $783\text{ cm}^{-1}$  shows the C-Cl stretching of halo compounds. The  $-\text{ONO}_2$  stretching vibrations appeared between  $700\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  at low-intensity absorption bands. At peak  $2216\text{ cm}^{-1}$  is a  $\text{C}\equiv\text{N}$  stretching of nitrile group present.



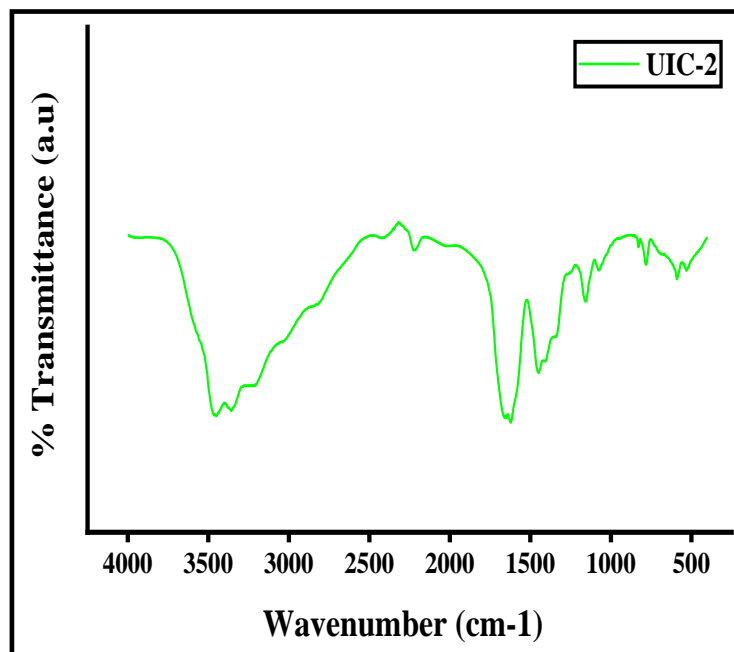


Figure 4.2- 7. FTIR Spectrum Of UIC-2.

The FTIR spectrum of UIC-3 was given in Figure. 4.2-8. At peak  $3936\text{ cm}^{-1}$ , urea shows O-H stretching vibrations. At wavelength  $3460\text{ cm}^{-1}$  and  $3363\text{ cm}^{-1}$  UIC-3 shows N-H and O-H stretching vibration like untreated one. At peak  $3256\text{ cm}^{-1}$ , the sample shows an O-H vibration, which implied water that is absorbed. The peak at  $2009\text{ cm}^{-1}$  is an Alkyne ( $\text{C}\equiv\text{C}$ ) stretching vibration. At peak  $1623\text{ cm}^{-1}$  is a Carbonyl ( $\text{C}=\text{O}$ ) stretching mode of carbon atom and keto ( $\text{C}=\text{O}$ ) group. The peak of  $1453\text{ cm}^{-1}$  is a bending vibration NH and CH stretching vibration of  $\text{O}=\text{C}-\text{NH}_2$ . Also, the band which appeared at  $1453\text{ cm}^{-1}$  is attributed to with  $\text{P}=\text{O}$  and  $-\text{CN}$  stretching. The band which appeared at  $1158\text{ cm}^{-1}$  is associated with  $\text{P}-\text{OH}$  stretching vibration. At  $1158\text{ cm}^{-1}$ , a stretching vibration mode resultant from the  $-\text{C}-\text{O}-\text{C}$  group can be seen like in untreated urea prill. C-H overtone stretching vibrations are observed at  $1158\text{ cm}^{-1}$ . The peaks from  $532\text{ cm}^{-1}$  to  $781\text{ cm}^{-1}$  shows the C-Cl stretching of halo compounds. At wavelength  $560\text{ cm}^{-1}$  shows  $\text{PO}_4$  vibration. The O-N=P and  $-\text{ONO}_2$  stretching vibrations appeared between  $700\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  at low-intensity absorption bands.

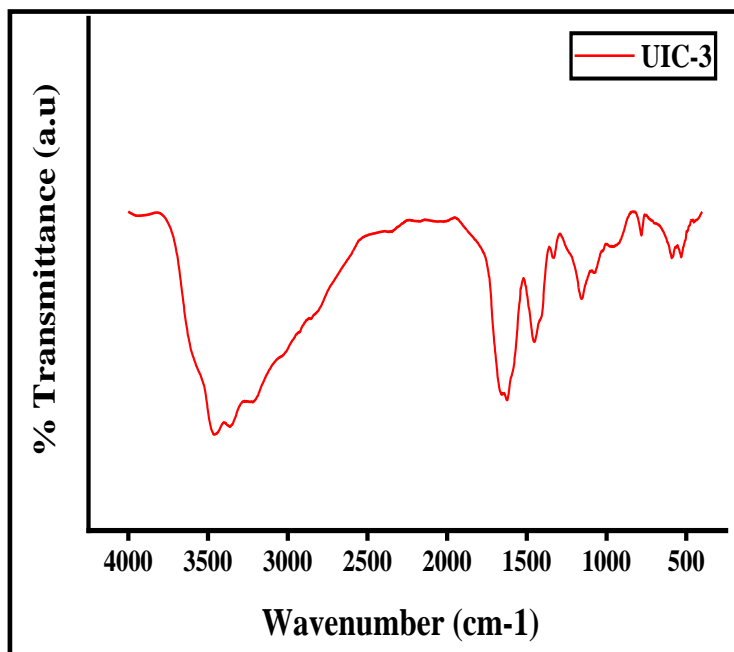


Figure 4.2- 8. FTIR Spectrum Of UIC-3.

### 4.2.3 Crushing Strength

If urea crystals fracture after treatment, the availability of nutritional nitrogen will be equivalent to that of untreated urea prills [82]. Samples with greater impact resistance against all odd pressures will be preferable in terms of storage, bagging, and shipping. Diverse ionic co-crystals materials were applied to urea in this work, and they were examined by applying pressure on it using a tensile tester until it broke.

Table 4. 3. Crushing Strength Of Untreated Urea And Urea Ionic Co-Crystals.

Samples	Crushing Strength (N)
Urea	16.18 ± 0.17
UIC-1	44.07 ± 0.44
UIC-2	214.71 ± 2.15
UIC-3	198.36 ± 1.98

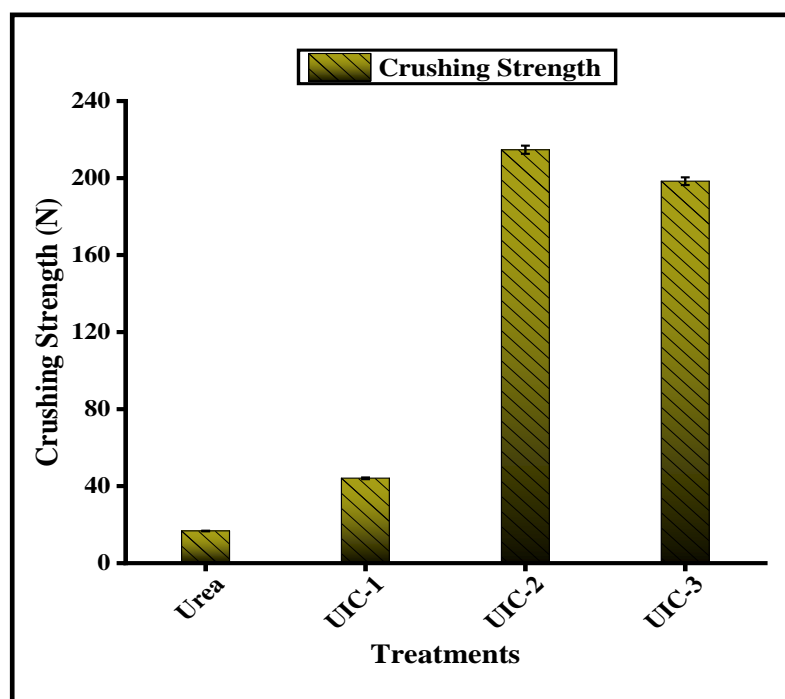


Figure 4.2- 9. Crushing Strength Of Untreated Urea And Urea Ionic Co-Crystals.

Figure. 4.2-9. and Table. 4.3. depicted the crushing strength outcomes following a transit through a universal testing machine. The final reading was taken when the urea globules were completely squashed into wispy powder, . Untreated prills mangled at a force of 16.68 N. UIC-2 showed elevated squashing power. This is due to ionization of nitric acid so hydrogen cation will attract towards the oxygen and forms covalent bond and as a result the formation of ionic bond when electronegative nitrate ion attracts towards the H bond.

#### 4.2.4 X-Ray Diffraction (XRD)

For the examination of crystalline characteristics of laboratory manufactured control release urea fertiliser, XRD was an effective approach. XRD patterns of the urea and parent compounds, e.g.  $ZnCl_2$ ,  $KCl$ , Urea Nitrate, and Urea Phosphate as well as replicated and experimental of  $Urea.ZnCl_2.KCl$ ,  $Urea.ZnCl_2.KCl.Urea$  Nitrate, and  $Urea.ZnCl_2.KCl.Urea$  Phosphate are shown in Figure. 4.2-10. All treatments reactant XRD patterns exhibit characteristic peaks and is more complex.

XRD pattern shown in Figure. 4.2-10. of  $CO(NH_2)_2 \cdot H_3PO_4$  consistent with the replicated trend relying on statistics of crystal structure [39], along with that of  $CO(NH_2)_2 \cdot 2HNO_3$  formed [39]. Solid  $H_2SO_4$ ,  $CO(NH_2)_2$  and  $H_2SO_4 \cdot 2CO(NH_2)_2$  accumulating from the leach urea  $H_2SO_4 \cdot H_2O$  mixture were seen by Dalman at 10 and

25 °C. The crystal structure of  $\text{H}_2\text{SO}_4 \cdot 2\text{CO}(\text{NH}_2)_2$  was not discovered prior to 1999, when Chen et al. discovered that the crystal form is made up of two uranium ions,  $\text{CO}(\text{NH}_2)_2\text{H}^+$  coupled to nearby  $\text{SO}_4^{2-}$ .

The growth of their crystals took place in a nitrogen atmosphere and were extremely soluble in both organic and inorganic solvents. The peaks had a high crystallinity, indicating that a clear compaction had developed with the urea granular.

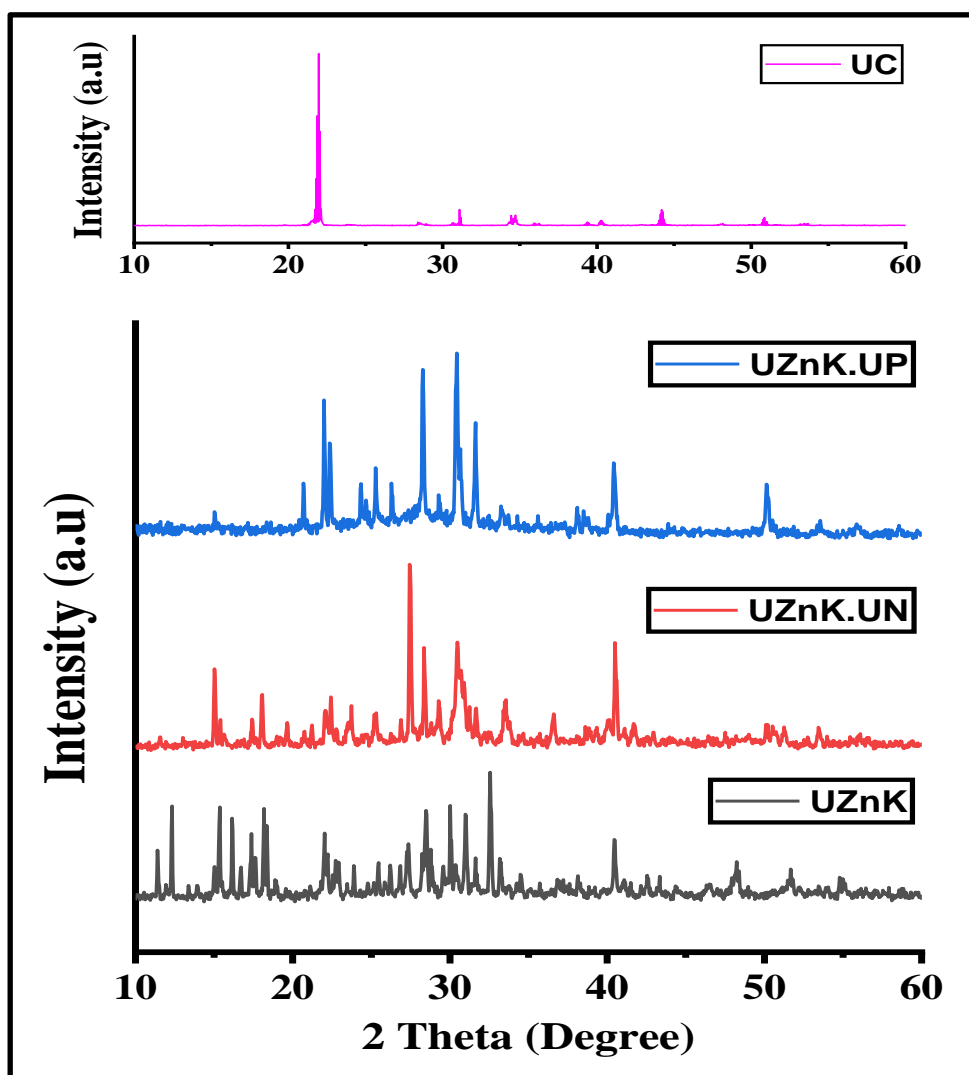


Figure 4.2- 10. XRD Pattern Of Untreated Urea & Urea Ionic Co-Crystals.

### 4.3 Soil Analysis

#### 4.3.1 Soil Moisture Content

Soil testing was performed at Barrani Agriculture Research Institute (BARI) in Chakwal. Soil was sandy loam type. 100 grams of 5 samples were taken from different

bags for testing the moisture content before starting the experimentation. The moisture content, and moisture factor was calculated by using following equations:

$$\text{Soil Moisture } (\Theta) = \frac{\text{Wet Soil (g)} - \text{Dry Soil (g)}}{\text{Wet Soil (g)}} \dots\dots (19)$$

$$\text{Moisture Factor} = \frac{\text{Wet Soil (g)}}{\text{Dry Soil (g)}} \text{ or, } \frac{100 + \% \Theta}{100} \dots\dots (20)$$

The results are presented below in Table. 4.4.

Table 4. 4. Soil Moisture Content.

S. No.	Weight Of Fresh Soil Samples (g)	Weight Of Soil After Drying (g)	Moisture Content (Θ) (g)	% Moisture Content	Moisture Factor
01	300	277	23	7.67	1.083
02	300	278	22	7.33	1.079
03	300	281	19	6.33	1.068
04	300	275	25	8.33	1.091
05	300	274	26	8.67	1.095
Average	300	277	23	7.67	1.083

### 4.3.2 Water Holding Capacity

Following equation gave the Water holding capacity (WHC)

$$100\% \text{ Water Holding Capacity} = \frac{w_1 - w_2}{w_2} \times 100 \dots\dots (21)$$

The results are presented as follows:

Table 4. 5. Water Holding Capacity.

S. No.	Weight Of Wet Soil After Drainage (W <sub>1</sub> )	Weight Of Oven Dry Soil (W <sub>a</sub> ) + Weight Of Pot (W <sub>b</sub> ) = (W <sub>2</sub> )	100% WHC = $\frac{w_1 - w_2}{w_2} \times 100$
01	320	254	25.98%
02	334	266	25.56%
Mean	327	260	25.77%

So, ml of water required for 2 kg pot =  $2000 \times 0.2577 = 515.4$  ml

For, 65% WHC:  $515.4 \times 0.65 = 335$  ml

### 4.3.3 pH Of Soil

Upon 65 days of planting spinach, a minor reduction in soil pH was observed, as indicated in Figure. 4.3-1. In comparison to the initial pH value of soil, urea ionic co-crystals showed a small increment of 0.21 units. A decrease of 0.09 unit was noted when the control value was compared to the average of all types of fertiliser supplied to the soil. There's was slight increment of 0.10 units in soil pH when matching the untreated urea pH value to the mean of all given coated fertilizer. In UIC-1 and UIC-2, there was a 0.15 unit increase in soil pH when comparing untreated urea to all other treated fertilisers. The pH value drops 0.05 units in UIC-3. All of the specimens had a pH of 7-8, which was neutral. The pH of the soil is not affected by urea or urea ionic co-crystals. The change in pH indicates a change in soil composition, and the treatment is not suited for long-term use since it will alter the composition and efficiency of nutrient transport to the soil. The outcome is consistent with the literature and previous investigations [109, 110]. The ANOVA results of pH are shown as:

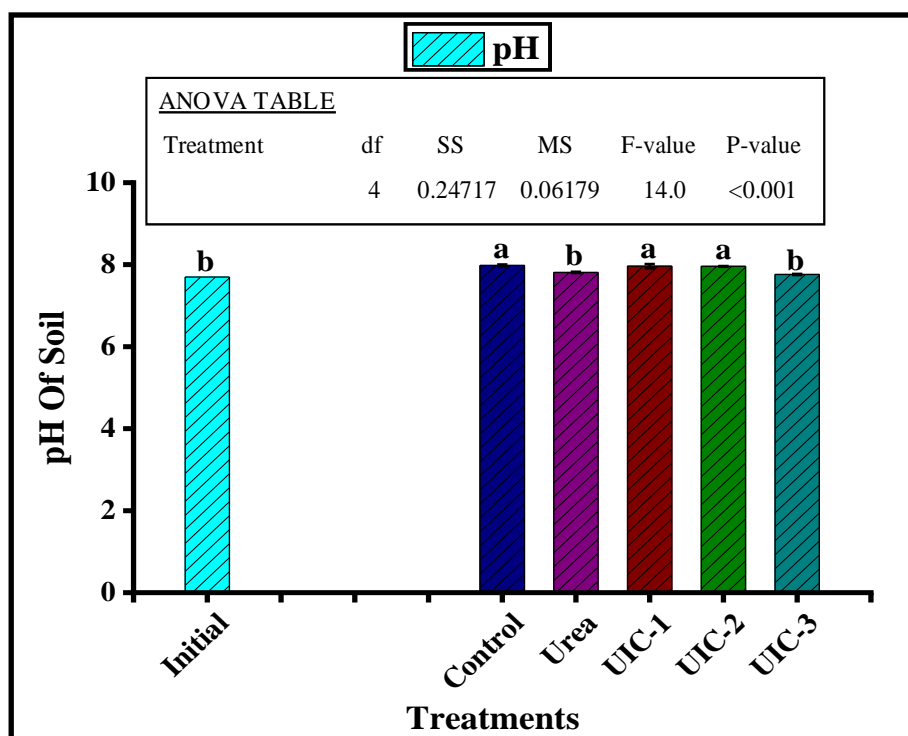


Figure 4.3- 1. pH Of Soil After The Application Of Urea & Urea Ionic Co-Crystals After 65 Days Of Planting Spinach.

#### 4.3.4 Electrical Conductivity (EC) Of Soil

The findings for soil EC is depicted in Figure. 4.3-2. In comparison to the initial soil, all applications demonstrated An improvement in soil EC. In comparison to the preliminary value, a unit increment of 0.14 dS/m in UIC-1 urea fertilizer, 0.09 dS/m in UIC-2 urea fertilizer, and 0.15 dS/m in UIC-3 urea fertilizer was observed on average. When the control figure was matched with the mean of supplied fertiliser to all treatments, a 0.05 dS/m rise was recorded. A drop of 0.09 dS/m was noticed when the untreated urea value was compared to the mean of soil with all treated fertilizer. The EC of the soil is not affected much by urea or urea ionic co-crystals. The change in EC indicates a change in soil composition, and the treatment is not suited for long-term use since it will alter the composition and efficiency of nutrient transport to the soil. The ANOVA results of EC are shown as:

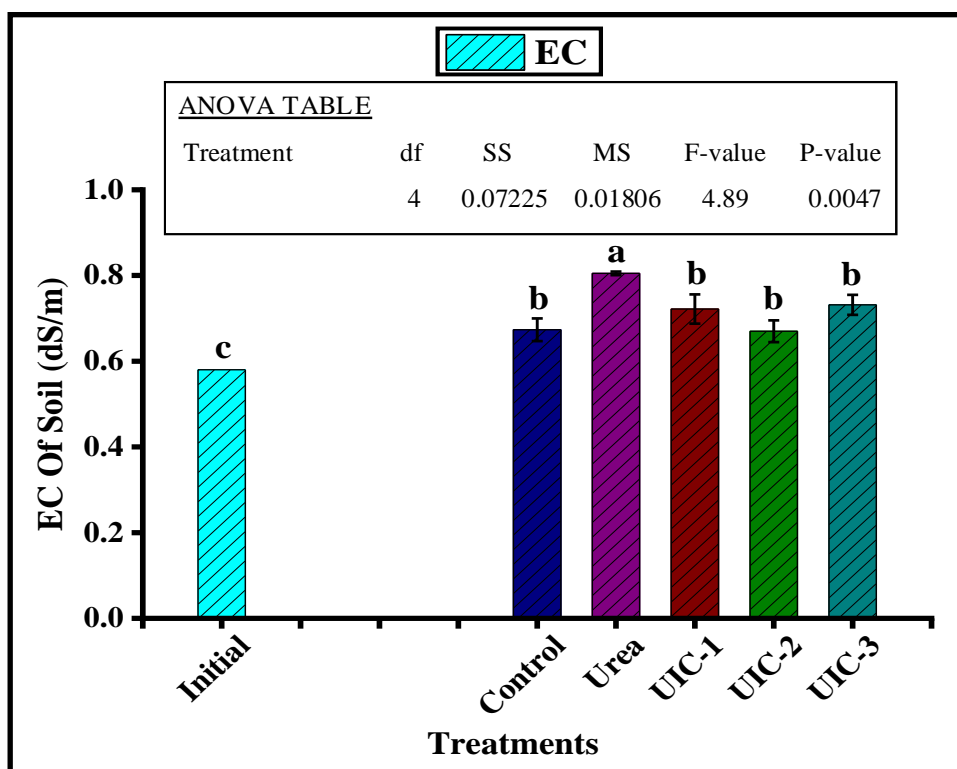


Figure 4.3- 2. Electrical Conductivity (EC) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.5 Total Organic Carbon (TOC) Of Soil

The availability of organic substances and microbes present in the soil that can transform ammonia to nitrogen for plants is indicated by the Organic Content. Figure. 4.3-3. depicts the effect of urea fertiliser and various types of ionic co-crystals urea

fertiliser on total organic carbon in soil. The application of fertiliser resulted in a large increase in TOC of the soil. When the initial soil %TOC (0.30%) value was compared to the average of all urea ionic co-crystals fertilizer an increment of 40.43% TOC was noted. When the control value was compared to the average of all other applied fertiliser treatments, a 22.58 percent increase was found. UIC-3 urea co-crystals have the greatest value (8.91 Mg/hac) followed by UIC-2 urea co-crystals (8.78 Mg/hac). When the value of untreated urea was compared to the average of ionic co-crystals treatments, a 14.86 percent rise was found. Organic acid is produced from available carbon. The higher the amount of accessible C, the more nutrients are produced in a disposition that can be conveniently sucked up by the plants. The higher the plant's nutrient absorption, the greater the output of plant fresh matter [103]. The ANOVA results of TOC are shown as:

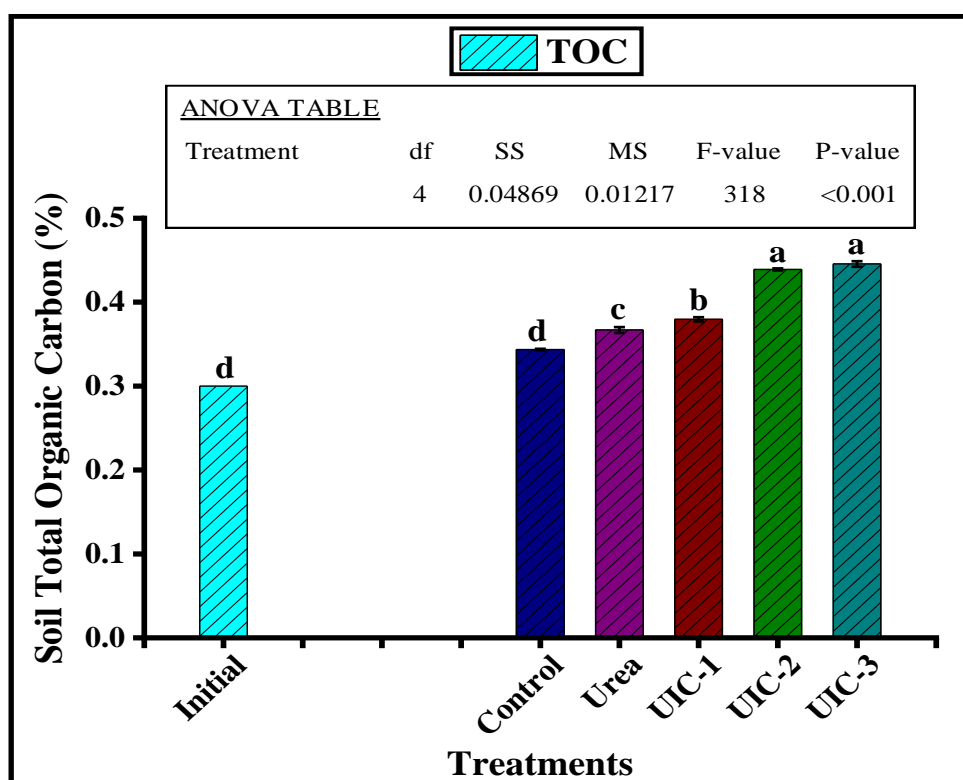


Figure 4.3- 3. Total Organic Carbon (TOC) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.6 Organic Matter (OM) Of Soil

Figure. 4.3-4. indicated the Organic Matter of soil that was computed from the total organic carbon of soil with the help of formula given below:

$$\% \text{ Organic Matter} = 1.724 \times (\% \text{ Total Organic Carbon}) \dots (22)$$



The application of fertiliser resulted in a large increase in OM of the soil. When the initial soil %OM (0.52%) was compared to the average of all urea ionic co-crystals fertilizer an increment of 39.69 % OM was noted. When the control value was compared to the average of all other applied fertiliser treatments, a 22.66 percent increase was found. UIC-3, have the greatest % OM (0.77%) followed by C-2 urea co-crystals (0.76%). When the value of untreated urea was compared to the average of ionic co-crystals treatments, a 14.86 percent rise was found.

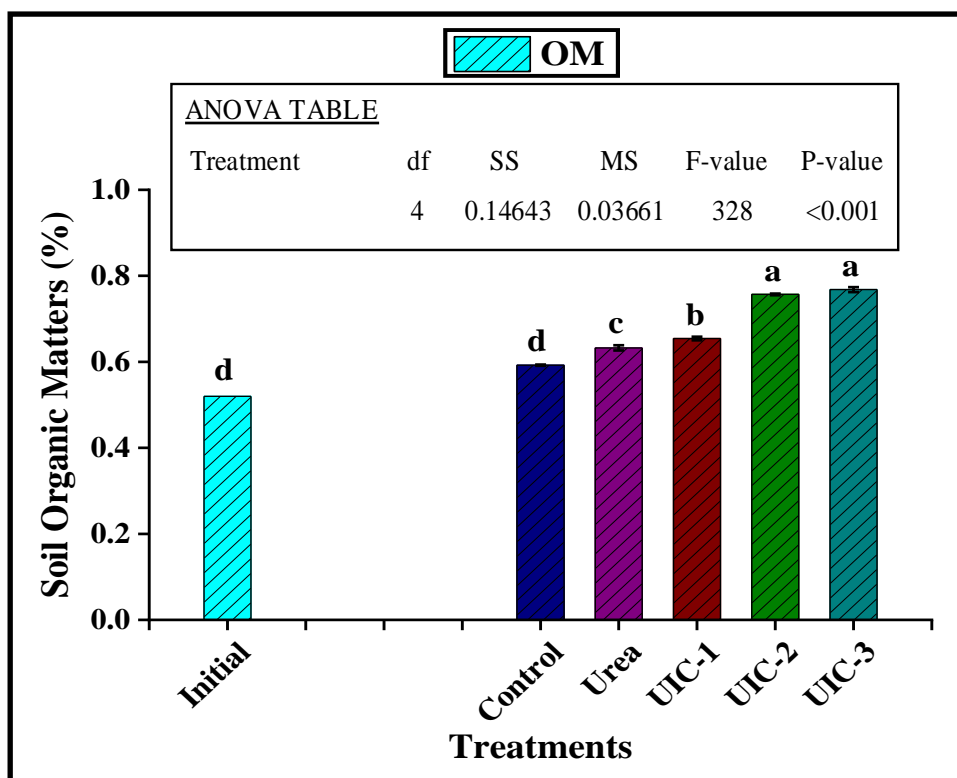


Figure 4.3- 4. Organic Matter (OM) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.7 Microbial Biomass Carbon (MBC)

The existence of microbial carbon mass is represented by MBC. Microbes having the C organism as their main source, which is in the form of permanent carbon, make up the microbial mass. Figure. 4.3-5. depicts information on microbial biomass C. It is noticeable that there has been a large rise in microbial (C). UIC-3 showed the greatest rise in microbial C, followed by UIC-2. This is due to fertiliser absorption. Growth of bacteria rises when soil C raises, increasing nutritional accessibility to crops. So when control value was compared to the average of all other treatments, a 127.97 percent rise was noted. When comparing the untreated urea value to the average of the other

ionic co-crystals fertiliser treatments, a 73.80 percent increase was seen [103]. The ANOVA results of MBC are shown as:

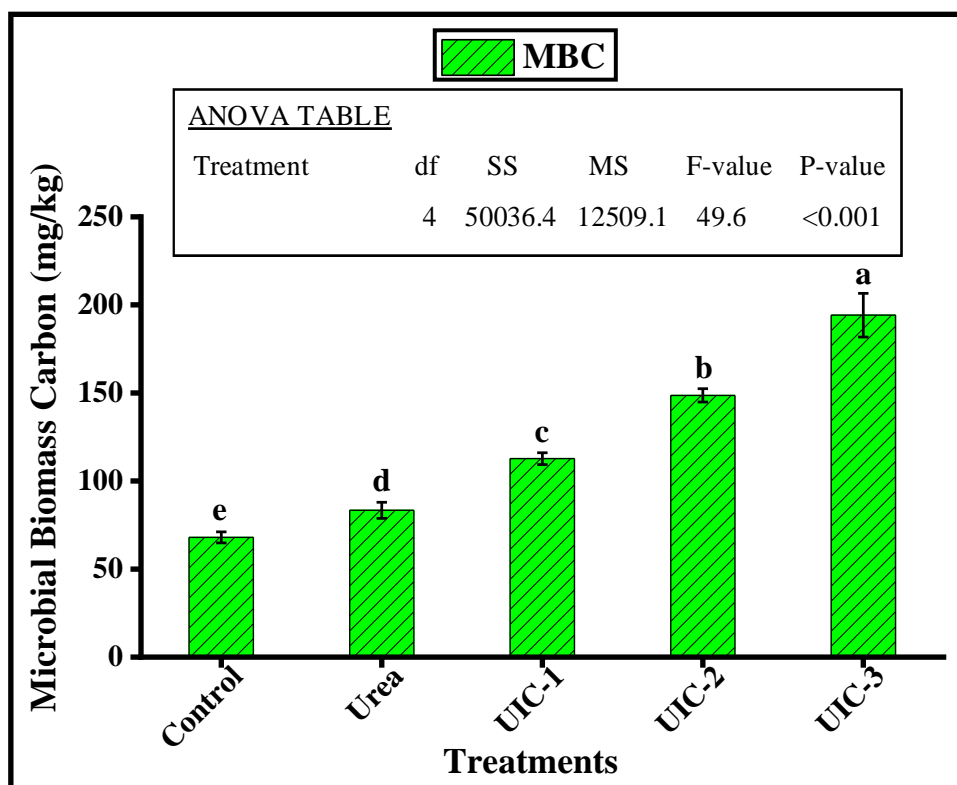


Figure 4.3- 5. Microbial Biomass Carbon (MBC) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.8 Microbial Biomass Nitrogen (MBN)

The existence of microbial nitrogen mass is indicated by MBN. As bacteria proliferate, the amount of microbial nitrogen produced increases.. The increment in microbial N was observed, as can be seen in Figure. 4.3-6. UIC-3 urea had the highest increase in microbial N, followed by UIC-2. Soil mineralization boosts the accessibility of N to crops, leading to a rise in microbial N. Bacterial bodies die when N levels rise, leading the formation of organic acid, that finally changes to plant-available N. So when mean of all ionic co-crystals treatments was matched with control value, there was a 122.14 percent rise. When the mean of all ionic co-crystals urea fertiliser treatments is matched with untreated urea, a 77.75 percent rise was recorded. In terms of plant dry matter yield data, these results are satisfactory [111].

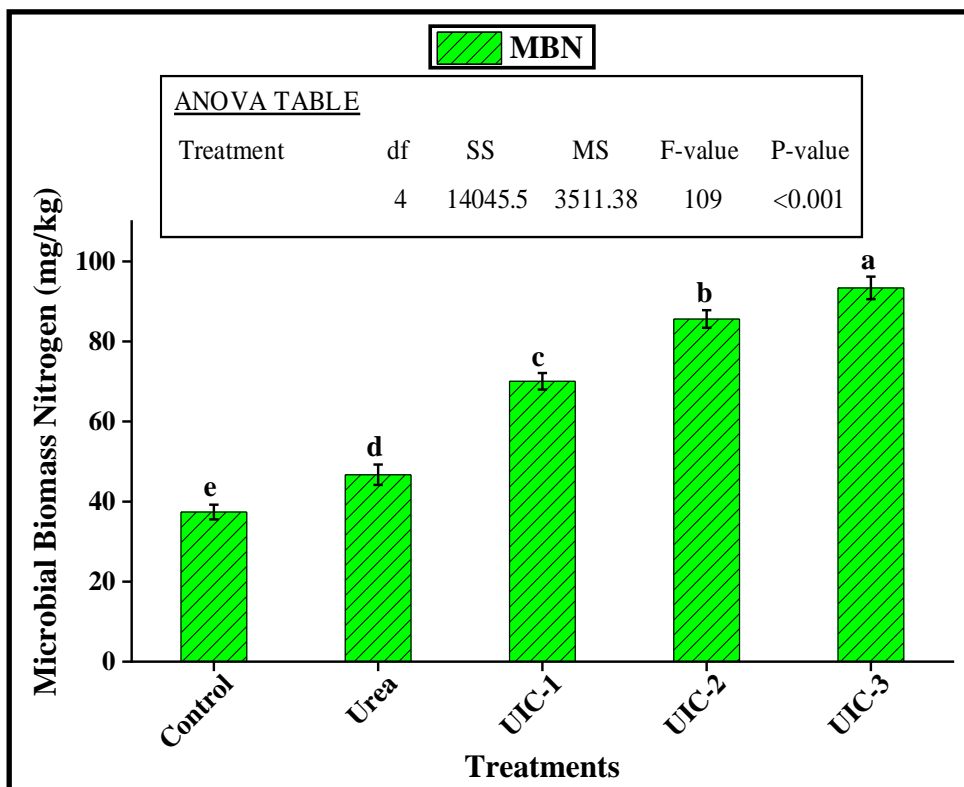


Figure 4.3- 6. Microbial Biomass Nitrogen (MBN) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.9 Microbial Biomass Phosphorus (MBP)

The presence of microbial phosphorous material is indicated by MBP. Figure. 4.3-7. depicts information on microbial biomass P. A considerable rise in microbial biomass P was clearly observed. UIC-3 demonstrated the highest rise in microbiological P, followed by UIC-2. So when control value was matched with mean of all other treatments, a 211.28 percent rise was recorded. By comparing the untreated urea value to the mean of the other ionic co-crystals treatments, a 75.50 percent rise was observed [96].

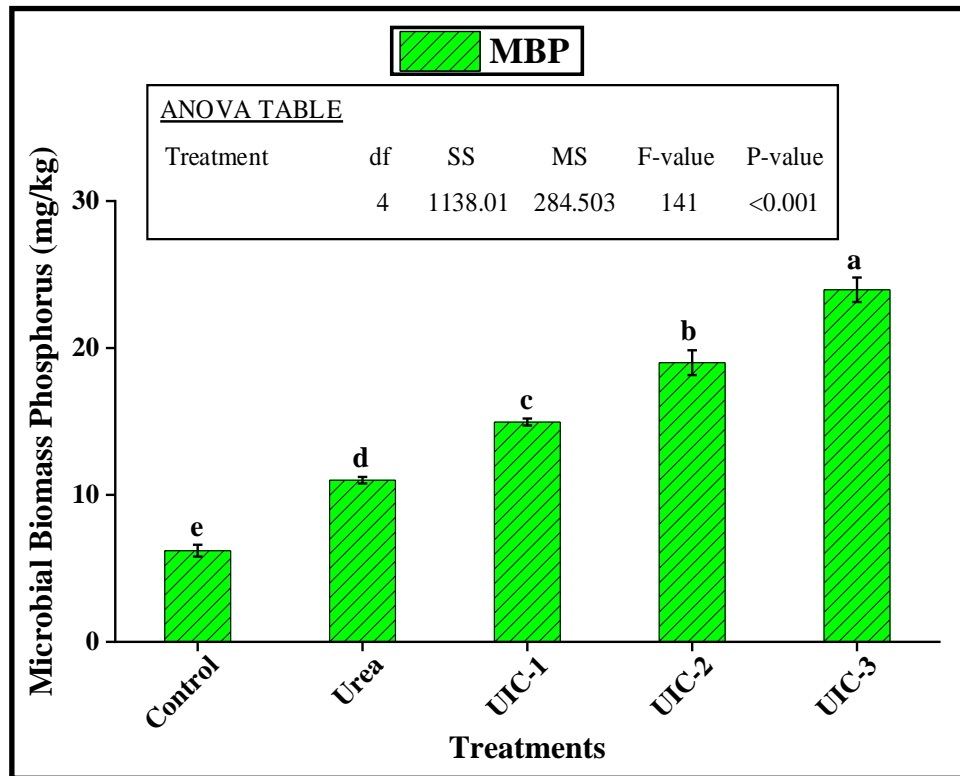


Figure 4.3- 7. Microbial Biomass Phosphorus (MBP) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.10 Microbial Biomass Potassium (MBK)

Microbial potassium mass is detected using MBK. Figure. 4.3-8. illustrates the microbial biomass K. There was a considerable rise in microbial biomass K. UIC-3 had the highest rise in microbiological K, followed by UIC-2. So when control value was compared to the mean of all other treatments, a 127.93 percent rise was found. When comparing the untreated urea value to the mean of the other ionic co-crystals treatments, a 60.91 percent rise was observed [97].

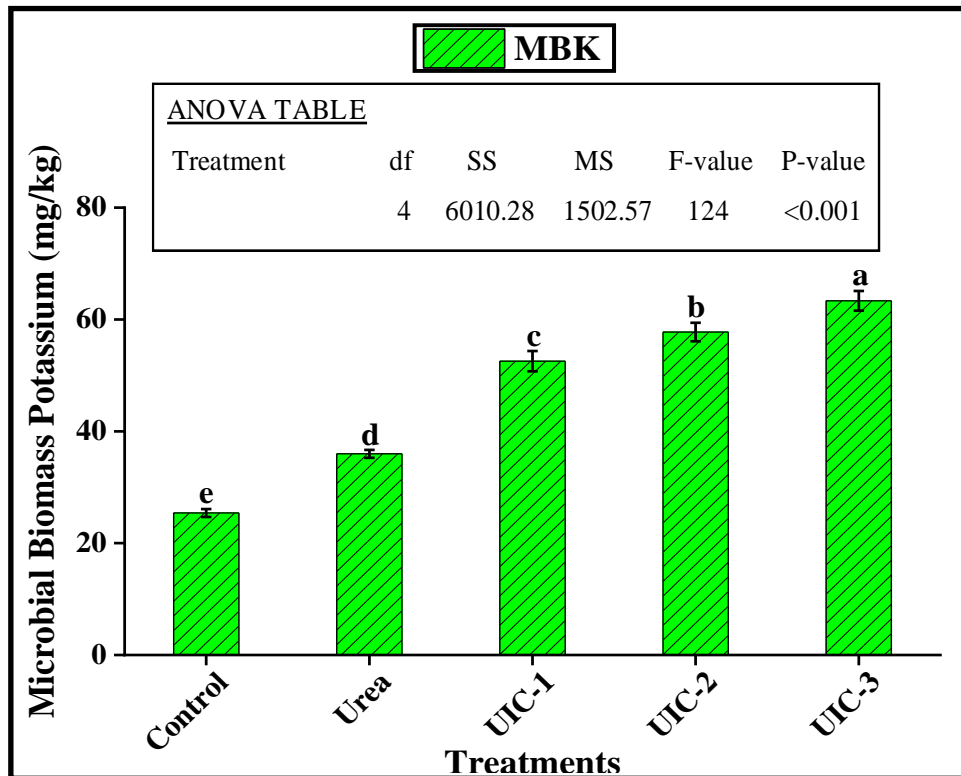


Figure 4.3- 8. Microbial Biomass Potassium (MBK) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.11 Mineral Nitrogen

Mineral Nitrogen are found as Nitrate-Nitrogen and Ammonium-Nitrogen. Ammonium-Nitrogen and Nitrate-Nitrogen are two main types of mineral nitrogen. In soils, ammonium ions are formed by the degradation of organic matter, manures, urea, or ammonium-containing fertilisers. The final state of nitrogen breakdown/reaction are nitrate ions (eliminating gaseous forms of N). The soil can be supplied with it by fertilizers [87].

##### 4.3.11.1 Nitrate-Nitrogen ( $\text{NO}_3 - \text{N}$ )

Figure 4.3-9. and Figure. 4.3-10. illustrates the presence of nitrate-nitrogen in soil and leachate. It can be clearly observed that the concentration of nitrate-nitrogen increased with the application of fertilizers. If all of the treatments' results are evaluated, it's noticeable that UIC-3 urea ionic co-crystals has the best score. UIC-2 urea ionic co-crystals get the best value following UIC-3 urea ionic co-crystals. When the score of control treatment was matched with all of the urea ionic co-crystals treatments, an increment of 124.89 % and 121.93 % was recorded in soil and leachate respectively. When the value of untreated urea was matched with the mean of all compacted ionic

co-crystals fertiliser provided treatments, a 17.34 % and 26.09 % rise was noticed in soil and leachate respectively. The outcome is consistent with the fertiliser release rate study in the lab. It's because of the highest effectiveness of UIC-3 urea ionic co-crystals, that means that nutrients are released gently and efficiently by the plant. The remaining content exceeds the needs of crops and is presently accessible in the soil [112].

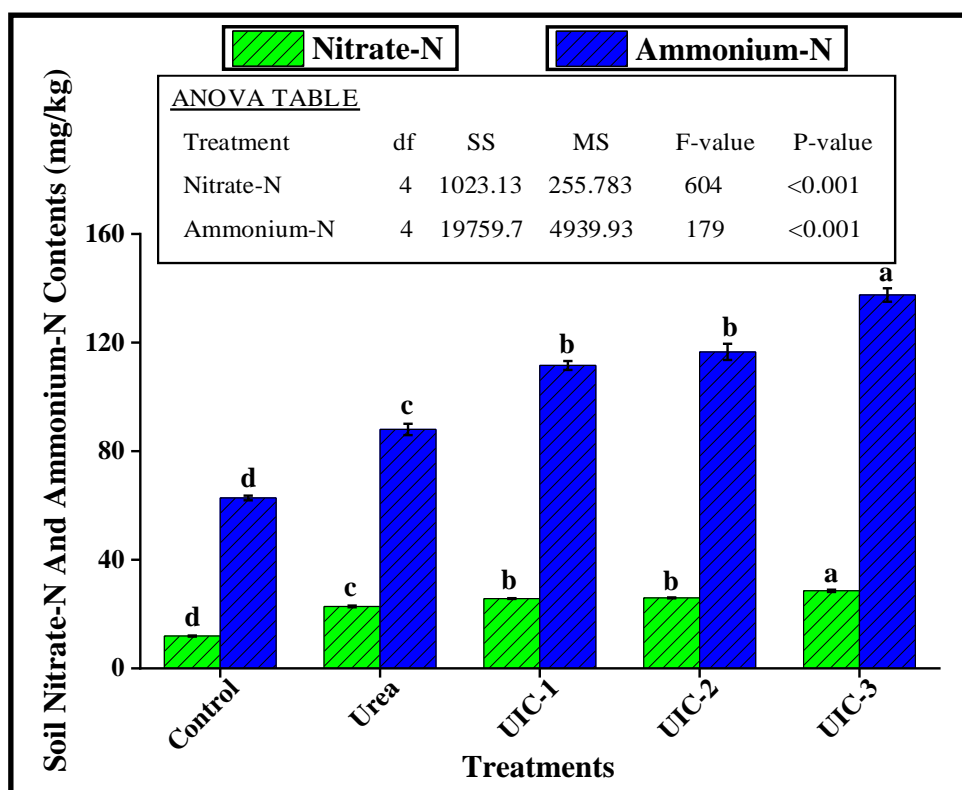


Figure 4.3- 9. Nitrate-N & Ammonium-N Contents In Soil After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.3.11.2 Ammonium-Nitrogen ( $\text{NH}_4^+$ -N)

Figure. 4.3-9. and Figure. 4.3-10. illustrates the presence of Ammonium-N in soil and leachate. It can be clearly observed that the concentration of Ammonium-N increased with the application of fertilizers. If all of the treatments' results are evaluated, it's noticeable that UIC-3 get the best value following UIC-2 urea ionic co-crystals. When the score of control treatment was matched with all of the urea ionic co-crystals treatments, an increment of 94.21 % and 191.20 % was recorded in soil and leachate respectively. When the value of untreated urea was matched with the mean of all compacted ionic co-crystals fertiliser provided treatments, a 38.51 % and 66.87 % rise

was noticed in soil and leachate respectively.. The outcome is consistent with the fertiliser release rate study in the lab. It's because of the highest effectiveness of UIC-3 and UIC-2 urea ionic co-crystals, that means that nutrients are released gently and efficiently by the plant. The remaining content exceeds the needs of crops and is presently accessible in the soil [112].

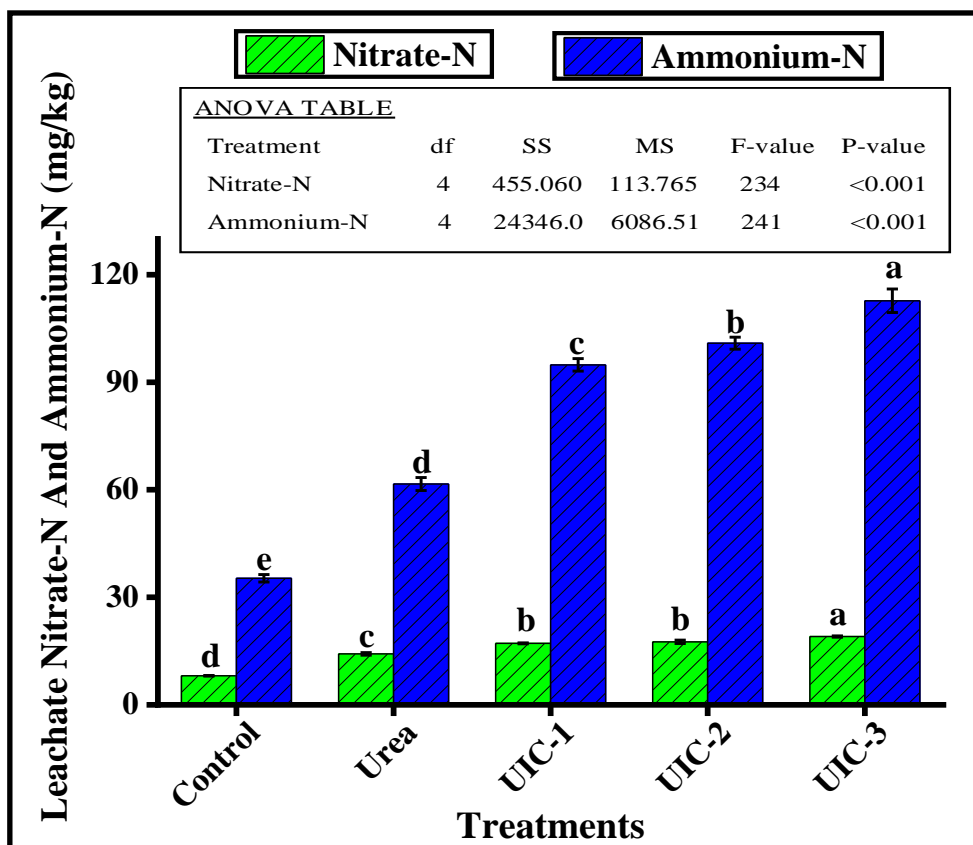


Figure 4.3- 10. Nitrate-N & Ammonium-N Contents In Leachate After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.4 Plants Analysis

In plants, shoots and roots analysis consist of Plant Height, Plant Diameter, Leaf Area, Fresh Matter Yield, Dry Matter Yield, Chlorophyll Contents, Plant Nitrogen Uptake, Apparent Nitrogen Recovery.

##### 4.4.1 Plant Height

The fertilizer's performance is measured by the plant's growth. The ANOVA findings in Figure. 4.4-1. indicate that the values of plant height for both harvestings presented in Table. 4.6. vary as the compacting materials alter, so the distinct UIC's fertilizers provide varied results in this study. For both harvestings, UIC-3 ( $23.15 \pm 0.64$ ) and

(13.26 ± 0.18) treatment yielded the best plant height, followed by UIC-2 (22.63 ± 0.38) and (13.01 ± 0.23). In the control sample, the lowest plant height was observed for both harvestings (16.27 ± 0.31) and (9.30 ± 0.20). The outcomes are consistent to existing studies [113].

Table 4. 6. Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Plant Height.

Treatments	Plant Height (cm) (1 <sup>st</sup> Harvest)	Plant Height (cm) (2 <sup>nd</sup> Harvest)
Control	16.27 ± 0.31	9.30 ± 0.20
Urea	19.15 ± 0.62	10.13 ± 0.23
UIC-1	20.97 ± 0.45	12.04 ± 0.23
UIC-2	22.63 ± 0.38	13.01 ± 0.23
UIC-3	23.15 ± 0.64	13.26 ± 0.18

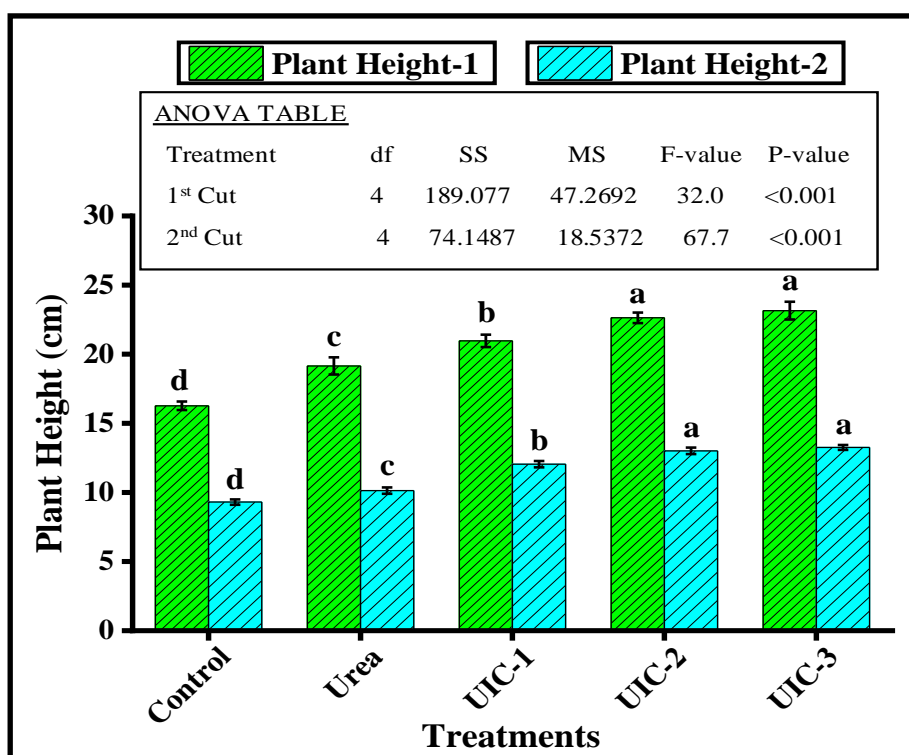


Figure 4.4- 1. Plant Height After The Application Of Urea And Urea Ionic Co-Crystals.

#### 4.4.2 Plant Diameter

The fertilizer's performance is measured by the plant's growth. The ANOVA findings in Figure. 4.4-2. indicate that the values of plant diameter for both harvestings presented in Table. 4.7. vary as the compacting materials alter, so the distinct UIC's



fertilizers provide varied results in this study. For both harvestings, UIC-3 ( $2.68 \pm 0.046$ ) and ( $1.60 \pm 0.014$ ) treatment yielded the best plant diameter, followed by UIC-2 ( $2.59 \pm 0.02$ ) and ( $1.56 \pm 0.018$ ). In the control sample, the lowest plant diameter was observed for both harvestings ( $1.91 \pm 0.024$ ) and ( $1.12 \pm 0.024$ ). The outcomes are consistent to existing studies [113].

Table 4. 7. Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Plant Diameter.

Treatments	Plant Diameter (mm) (1 <sup>st</sup> Harvest)	Plant Diameter (mm) (2 <sup>nd</sup> Harvest)
Control	$1.91 \pm 0.020$	$1.12 \pm 0.024$
Urea	$2.07 \pm 0.024$	$1.22 \pm 0.027$
UIC-1	$2.43 \pm 0.039$	$1.47 \pm 0.021$
UIC-2	$2.59 \pm 0.020$	$1.56 \pm 0.018$
UIC-3	$2.68 \pm 0.046$	$1.60 \pm 0.014$

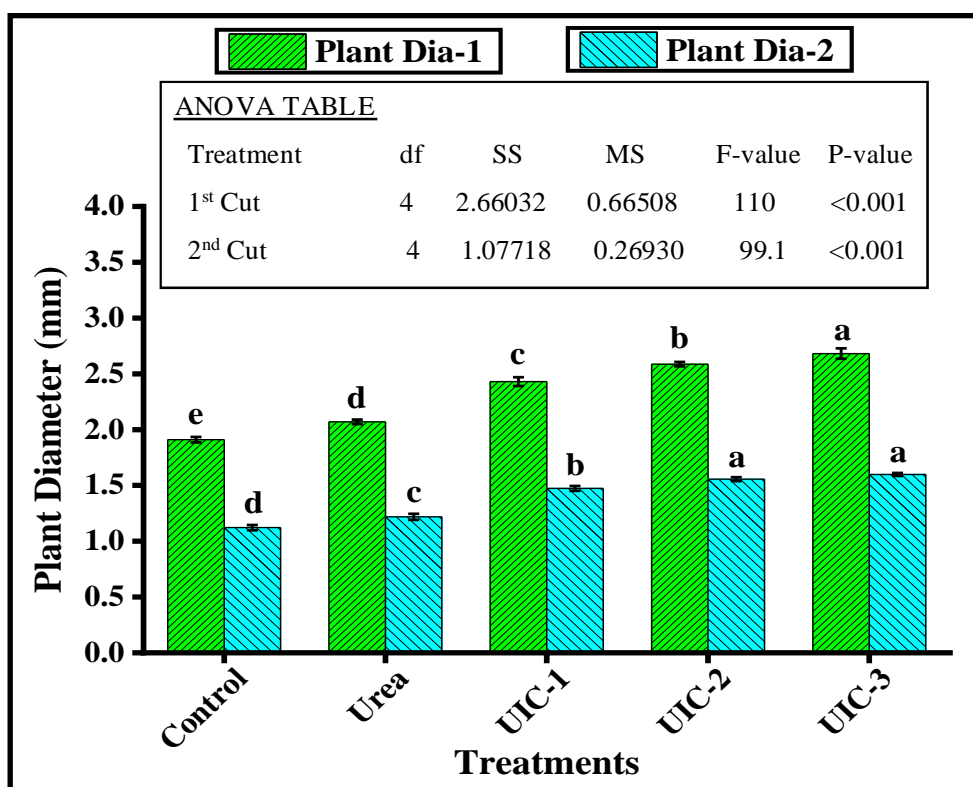


Figure 4.4- 2. Plant Diameter After The Application Of Urea And Urea Ionic Co-Crystals.

#### 4.4.3 Leaf Area And Leaf Area Index

The impact of urea and different forms of urea ionic co-crystals fertiliser on plant leaf area and leaf area index is illustrated in Table. 4.8. and Figure 4.4-3 (a) and (b) for both harvestings. UIC-3 treatment achieved the maximum leaf area ( $34601.10 \pm 597.280$ ) and ( $20623.03 \pm 177.59$ ) and leaf area index ( $3.460 \pm 0.060$ ) and ( $2.062 \pm 0.018$ ) for both harvestings respectively, followed by UIC-2 having leaf area ( $33536.65 \pm 258.58$ ) and ( $20182.495 \pm 228.68$ ) and leaf area index ( $3.35 \pm 0.026$ ) and ( $2.02 \pm 0.023$ ) for both harvestings respectively. In the control treatment, the least leaf area ( $9780.962 \pm 124.035$ ) and ( $5743.968 \pm 120.761$ ) and leaf area index ( $0.978 \pm 0.012$ ) and ( $0.574 \pm 0.012$ ) were measured for both harvestings respectively.

Table 4. 8. Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Leaf Area & Leaf Area Index (LAI).

Treatments	Leaf Area (cm <sup>2</sup> /m <sup>2</sup> ) (1 <sup>st</sup> Harvest)	Leaf Area Index (m <sup>2</sup> /m <sup>2</sup> )	Leaf Area (cm <sup>2</sup> /m <sup>2</sup> ) (2 <sup>nd</sup> Harvest)	Leaf Area Index (m <sup>2</sup> /m <sup>2</sup> )
Control	9780.96 ± 124.04	0.98 ± 0.01	5743.97 ± 120.76	0.57 ± 0.01
Urea	21408.93 ± 208.57	2.14 ± 0.02	12600.5 ± 283.14	1.26 ± 0.03
UIC-1	28714.37 ± 461.70	2.87 ± 0.05	17409.81 ± 252.82	1.74 ± 0.02
UIC-2	33536.65 ± 258.58	3.35 ± 0.03	20182.50 ± 228.68	2.02 ± 0.02
UIC-3	34601.10 ± 597.28	3.46 ± 0.06	20623.03 ± 177.59	2.06 ± 0.02

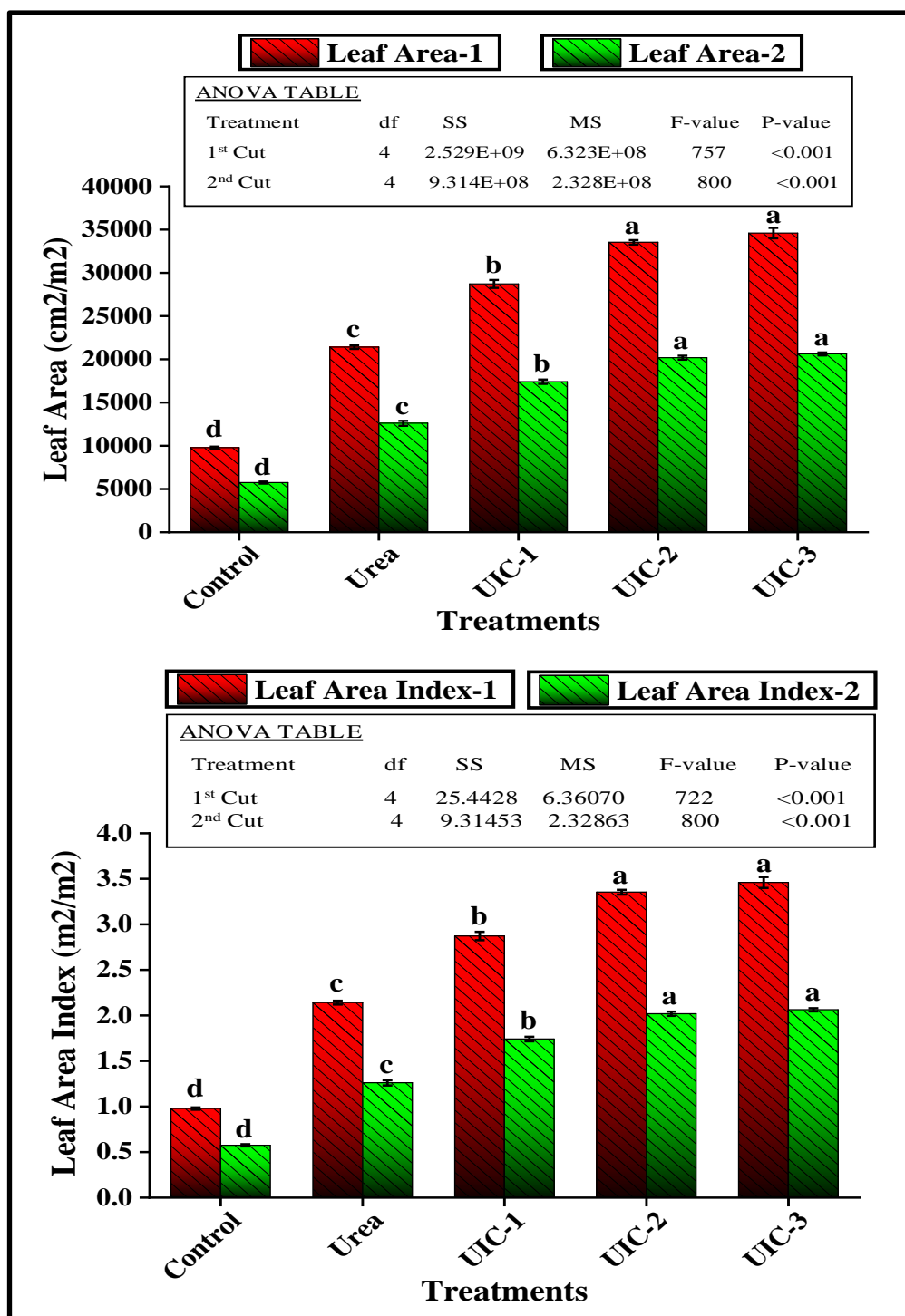


Figure 4.4- 3. Plant Diameter After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.4.4 Fresh Matter Yield Of Plant

##### 4.4.4.1 Spinach Fresh Mass Yield

Table. 4.9. and Figure. 4.4-4. illustrate the response of urea and various types of urea ionic co-crystals fertiliser on spinach fresh matter yield after both harvestings. After both harvestings, it was clear that the fresh mass yield of urea ionic co-crystal

treatments was the maximum. This also indicates the urea's slow and steady release. Moreover, after both harvestings, the UIC-3 treatment ( $28.58 \pm 2.01$ ) and ( $12.52 \pm 0.78$ ) respectively yields the highest spinach fresh matter yield, followed by UIC-2 treatment ( $26.09 \pm 0.67$ ) and ( $11.93 \pm 0.35$ ) respectively for both harvestings. The control treatment has the lowest spinach fresh matter yield ( $14.40 \pm 0.72$ ) and ( $7.64 \pm 0.37$ ) respectively for both harvestings. This is due to the absence of compacting materials with urea, that's result in rapid urea release.

Table 4. 9. Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Spinach Fresh Mass Yield.

Treatments	Spinach Fresh Mass Yield (g/pot) (1 <sup>st</sup> Harvest)	Spinach Fresh Mass Yield (g/pot) (2 <sup>nd</sup> Harvest)
Control	$14.40 \pm 0.72$	$7.64 \pm 0.37$
Urea	$21.93 \pm 1.20$	$10.43 \pm 0.28$
UIC-1	$22.20 \pm 0.65$	$11.30 \pm 0.70$
UIC-2	$26.09 \pm 0.67$	$11.93 \pm 0.35$
UIC-3	$28.58 \pm 2.01$	$12.52 \pm 0.78$

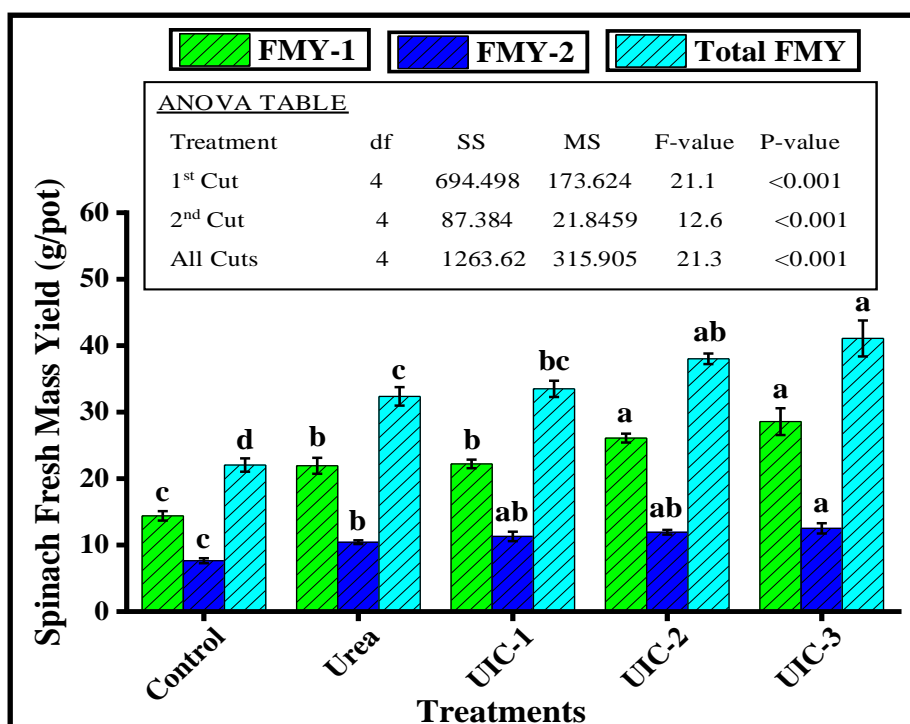


Figure 4.4- 4. Fresh Mass Yield Of Spinach After The Application Of Urea & UICs.

#### 4.4.4.2 Roots Fresh Mass Yield

Table. 4.10. and Figure. 4.4-5. illustrate the response of urea and various types of urea ionic co-crystals fertiliser on plant roots fresh matter yield. It was clear that the roots fresh mass yield of urea ionic co-crystal treatments was the maximum. This also indicates the urea's slow and steady release. Moreover, the UIC-3 treatment ( $21.81 \pm 0.33$ ) yields the highest roots fresh matter yield, followed by UIC-2 treatment ( $21.29 \pm 1.25$ ). The control treatment has the lowest roots fresh matter yield ( $15.24 \pm 0.33$ ). This is due to the absence of compacting materials with urea, that's result in rapid urea release.

Table 4. 10. Effect Of Urea & UIC's Fertilizer On Roots Fresh Mass Yield.

<b>Treatments</b>	<b>Roots Fresh Mass Yield (g/pot)</b>
<b>Control</b>	<b><math>15.24 \pm 0.33</math></b>
<b>Urea</b>	<b><math>20.26 \pm 0.57</math></b>
<b>UIC-1</b>	<b><math>20.87 \pm 0.22</math></b>
<b>UIC-2</b>	<b><math>21.29 \pm 0.33</math></b>
<b>UIC-3</b>	<b><math>21.81 \pm 1.25</math></b>

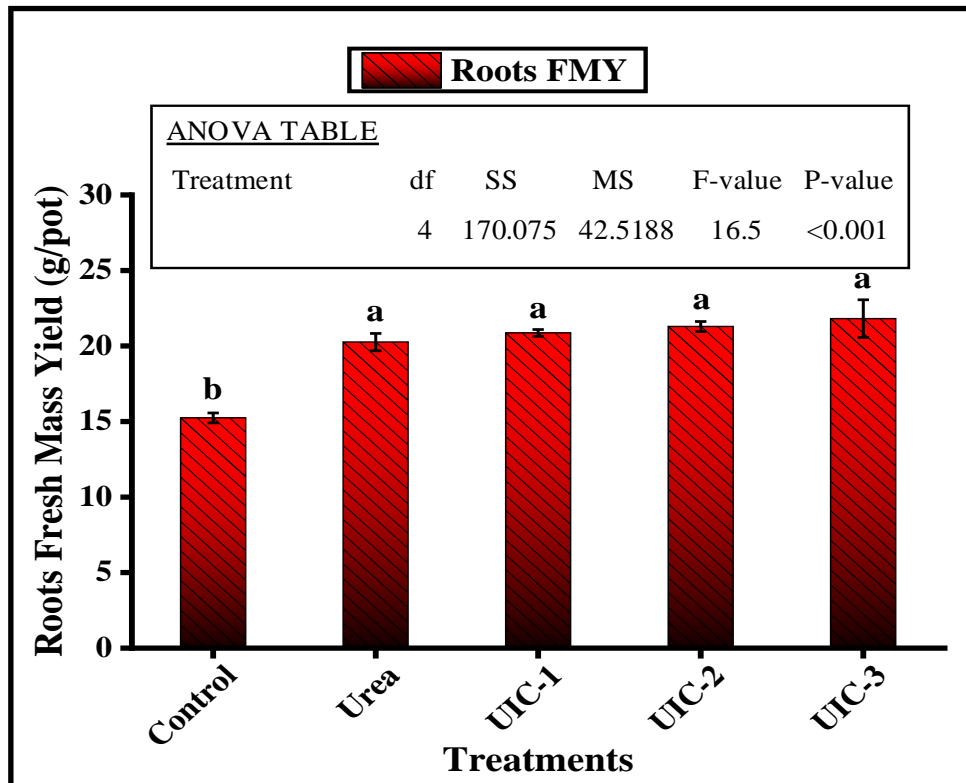


Figure 4.4- 5. Roots Fresh Mass Yield After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.4.5 Dry Matter Yield Of Plant

##### 4.4.5.1 Spinach Dry Mass Yield

Table. 4.11. and Figure. 4.4-6. illustrate the response of urea and various types of urea ionic co-crystals fertilizer on spinach dry matter yield after both harvestings. After both harvestings, it was clear that the spinach dry mass yield of urea ionic co-crystal treatments was the maximum. This also indicates the urea's slow and steady release. Moreover, after both harvestings, the UIC-3 treatment ( $1.43 \pm 0.11$ ) and ( $1.03 \pm 0.07$ ) respectively yields the highest spinach dry matter yield, followed by UIC-2 treatment ( $1.36 \pm 0.05$ ) and ( $1.00 \pm 0.04$ ) respectively for both harvestings. The control treatment has the lowest spinach dry matter yield ( $1.08 \pm 0.04$ ) and ( $0.63 \pm 0.03$ ) respectively for both harvestings. This is due to the absence of compacting materials with urea, that's result in rapid urea release.

Table 4. 11. Effect Of Urea & UIC's Fertilizer On Spinach Dry Mass Yield.

Treatments	Spinach Dry Mass Yield (g/pot) (1 <sup>st</sup> Harvest)	Spinach Dry Mass Yield (g/pot) (2 <sup>nd</sup> Harvest)
Control	1.08 ± 0.04	0.63 ± 0.03
Urea	1.30 ± 0.08	0.88 ± 0.02
UIC-1	1.35 ± 0.06	0.92 ± 0.05
UIC-2	1.36 ± 0.05	1.00 ± 0.04
UIC-3	1.43 ± 0.11	1.03 ± 0.07

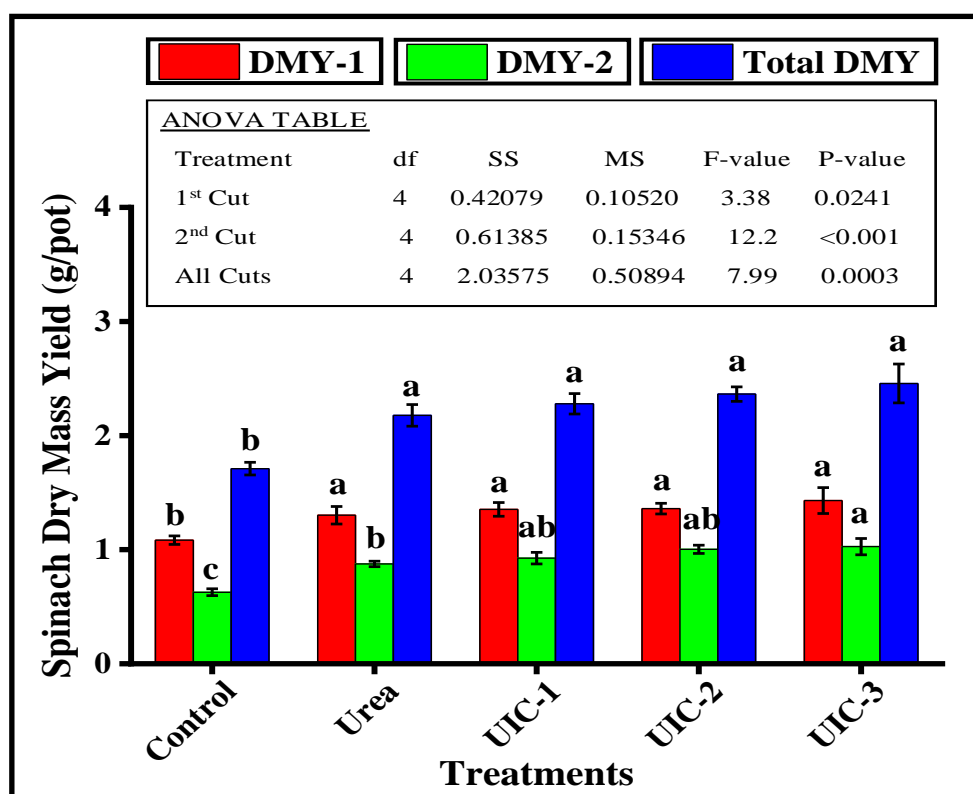


Figure 4.4- 6. Dry Mass Yield Of Spinach After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.4.5.2 Roots Dry Mass Yield

Table. 4.12. and Figure. 4.4-7. illustrate the response of urea and various types of urea ionic co-crystals fertiliser on plant roots dry matter yield. It was clear that the roots dry mass yield of urea ionic co-crystal treatments was the maximum. This also indicates

the urea's slow and steady release. Moreover, the UIC-3 treatment ( $3.89 \pm 0.22$ ) yields the highest roots dry matter yield, followed by UIC-2 ( $3.80 \pm 0.06$ ). The control treatment has the lowest roots dry matter yield ( $2.72 \pm 0.06$ ). This is due to the absence of compacting materials with urea, that's result in rapid urea release.

Table 4. 12. Effect Of Urea & UIC's Fertilizer On Roots Dry Mass Yield.

Treatments	Roots Fresh Mass Yield (g/pot)
Control	$2.72 \pm 0.06$
Urea	$3.61 \pm 0.10$
UIC-1	$3.72 \pm 0.04$
UIC-2	$3.80 \pm 0.06$
UIC-3	$3.89 \pm 0.22$

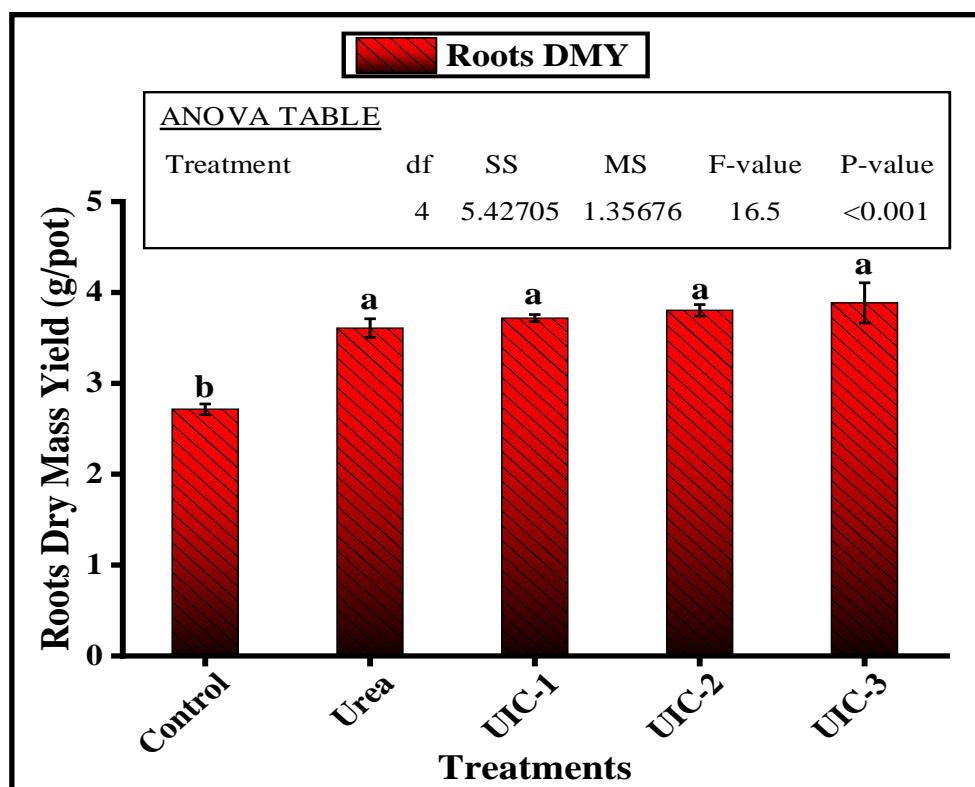


Figure 4.4- 7. Roots Dry Mass Yield After The Application Of Urea & Urea Ionic Co-Crystals.



#### 4.4.6 Chlorophyll Contents

The bulk of chlorophyll per unit area computes the photosynthetic potential of a plant. There is a straight relation between the soil's nitrogen availability and chlorophyll in plants. In fertilizer management, chlorophyll can be utilized as a secondary standard of levels of nitrogen.

##### 4.4.6.1 Chlorophyll Values Via SPAD Meter

Due to the slow and steady release of urea, urea ionic co-crystals treatments deliver the finest performances during both harvestings. UIC-3 has the best average plant chlorophyll, measuring  $(29.6 \pm 0.80)$  and  $(40.95 \pm 0.43)$  respectively for both harvestings and is followed by UIC-2  $(28.2 \pm 0.65)$  and  $(38.5 \pm 0.39)$  respectively for both harvestings. Control treatment gives a figure of  $(26.22 \pm 0.21)$  and  $(31.52 \pm 1.04)$  as the lowest value for both harvestings respectively. The ANOVA findings reveal that the values of chlorophyll vary when urea ionic co-crystals are applied, and that different outcomes can be obtained by employing different urea ionic co-crystals fertilisers in this experiment. Table. 4.13. and Figure. 4.4-8. depicts the chlorophyll content of all samples, during both harvestings.

Table 4. 13. Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Plant Chlorophyll Content.

Treatments	Plant Chlorophyll Content ( $\mu\text{g/g}$ ) (1 <sup>st</sup> Harvest)	Plant Chlorophyll Content ( $\mu\text{g/g}$ ) (2 <sup>nd</sup> Harvest)
Control	$26.22 \pm 0.21$	$31.52 \pm 1.04$
Urea	$26.57 \pm 0.40$	$37.12 \pm 0.27$
UIC-1	$27.15 \pm 0.56$	$37.88 \pm 0.64$
UIC-2	$28.20 \pm 0.65$	$38.50 \pm 0.39$
UIC-3	$29.60 \pm 0.80$	$40.95 \pm 0.43$

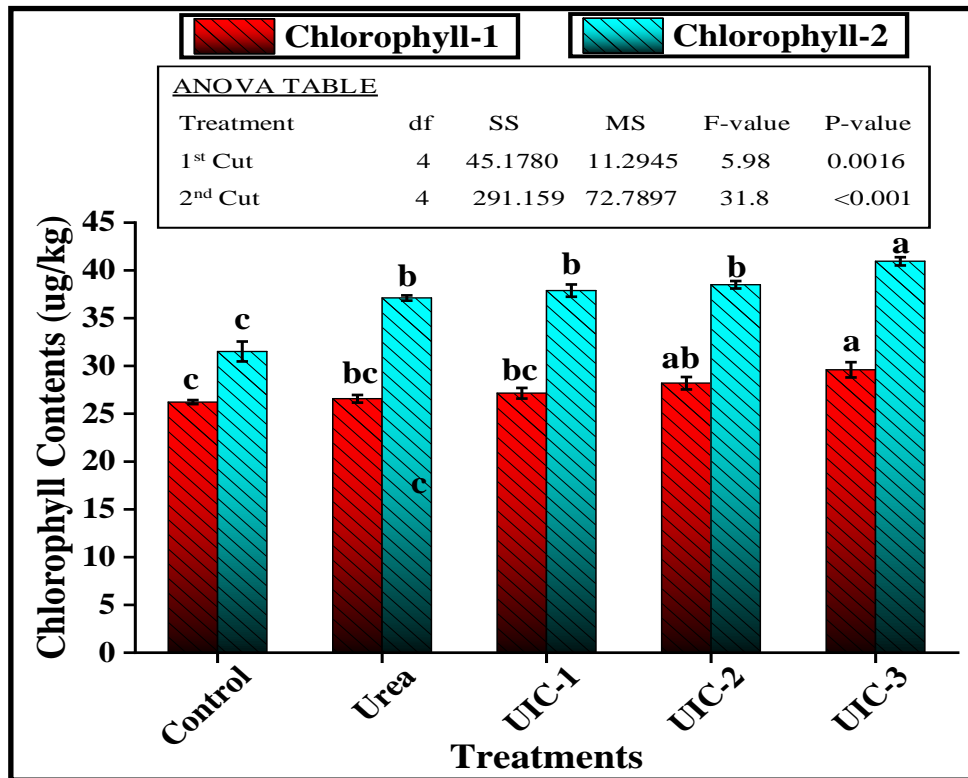


Figure 4.4- 8. Chlorophyll Contents After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.4.6.2 Chlorophyll Values a, b, and Total Chlorophyll

Due to the slow and steady release of urea, urea ionic co-crystals treatments deliver the finest performances during both harvestings. UIC-3 has the best average plant chlorophyll, measuring (30.48  $\mu\text{g/g}$ ), and is followed by UIC-2 (27.08  $\mu\text{g/g}$ ). Control treatment gives a figure of (19.33  $\mu\text{g/g}$ ) as the lowest value. The ANOVA findings reveal that the values of chlorophyll vary when urea ionic co-crystals are applied, and that different outcomes can be obtained by employing different urea ionic co-crystals fertilisers in this experiment. Table. 4.14. and Figure. 4.4-9. depicts the chlorophyll values a, b, and total chlorophyll of all samples, during both harvestings.

Table 4. 14. Chlorophyll a, b & Total After The Application Of Urea & UIC's.

Treatments	Plant Chlorophyll a (µg/g)	Plant Chlorophyll b (µg/g)	Total Chlorophyll (µg/g)
Control	12.49 ± 0.46	6.84 ± 0.12	19.33 ± 0.55
Urea	15.42 ± 0.55	7.84 ± 0.20	23.26 ± 0.74
UIC-1	17.56 ± 0.15	6.70 ± 0.17	24.25 ± 0.25
UIC-2	18.93 ± 0.98	8.16 ± 0.65	27.09 ± 0.80
UIC-3	19.54 ± 0.63	10.95 ± 0.60	30.48 ± 0.81

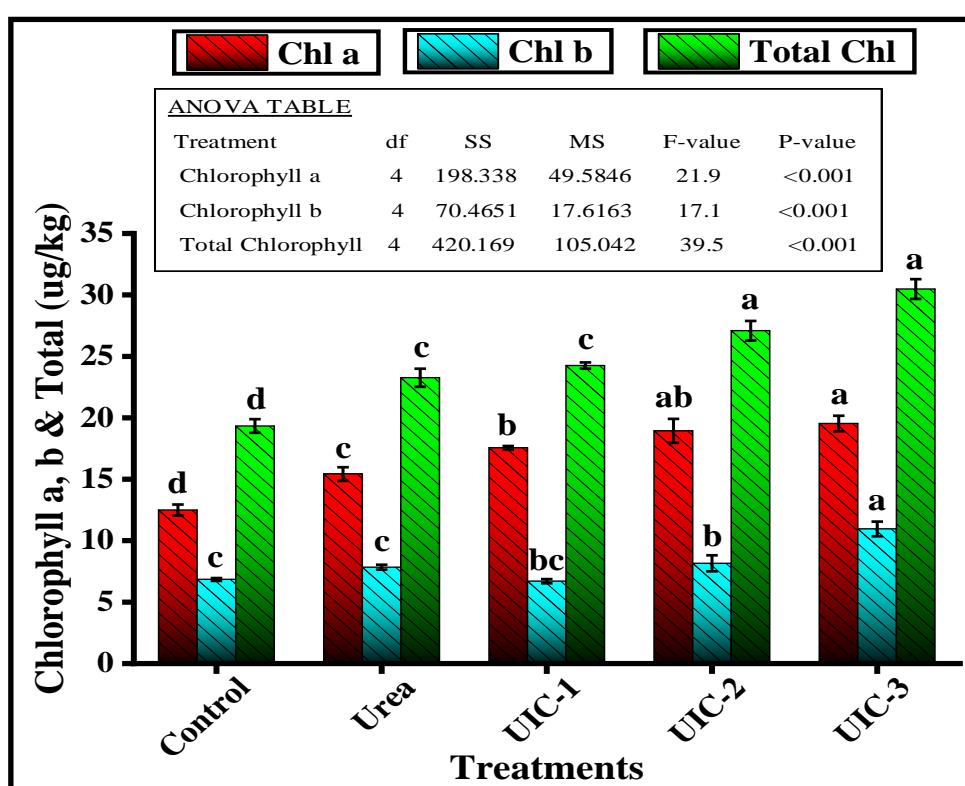


Figure 4.4- 9. Chlorophyll a, b & Total After The Application Of Urea & UICs.

#### 4.4.7 Nitrogen Uptake

The nitrogen content of the crops is represented via nitrogen uptake. Table. 4.15. and Figure. 4.4-10. provides data on plant uptake of nitrogen. In comparison to the control, urea fertiliser treatments showed a considerable increase in N uptake. In comparison to various urea ionic co-crystal fertiliser applied treatments, UIC-3 urea ionic co-crystals demonstrated the highest N uptake value after both harvestings. These findings

are similar to those of the release rate test. Ionic co-crystals of UIC-3 urea have the maximum N efficiency and release nutrients slowly, allowing the plant to easily uptake them. When comparing the findings, it can be shown that the average increase from the control value is 130.74 % and 188.73 % respectively after both harvestings. When comparing the average of UICs fertilizer to untreated urea value, there is a 109.02 % and 124.37 % rise respectively after both harvestings.

Table 4. 15. Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Plant Nitrogen Uptake.

Treatments	Plant Nitrogen Uptake (mg/kg) (1 <sup>st</sup> Harvest)	Plant Nitrogen Uptake (mg/kg) (2 <sup>nd</sup> Harvest)
Control	126.19 ± 6.28	72.44 ± 3.54
Urea	139.30 ± 7.60	93.22 ± 2.51
UIC-1	263.67 ± 7.76	181.64 ± 11.30
UIC-2	288.29 ± 7.43	214.24 ± 6.33
UIC-3	321.57 ± 22.65	231.62 ± 14.42

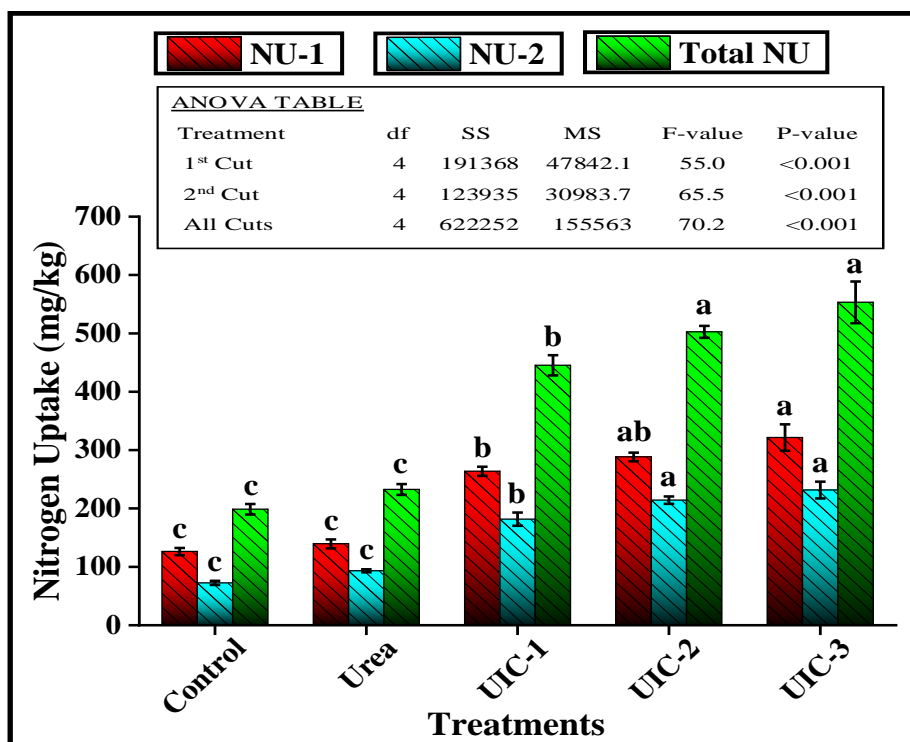


Figure 4.4- 10. Plant Nitrogen Uptake After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.4.8 Apparent Nitrogen Recovery

The nitrogen content of the plants gained from the fertilizer is indicated by Apparent Nitrogen Recovery (ANR). It demonstrates the fertilizer's effectiveness. UIC-3 had the highest ANR, with 64.30 % and 46.32 % percent respectively after both harvestings, followed by UIC-2 and UIC-1, with 57.66 % and 42.84 % percent respectively after both harvestings. Control treatment had the lowest value, with 25.24 % and 14.48 % respectively after both harvestings. The ANOVA results reveal that the values of ANR will change when urea ionic co-crystals applications alter, and that distinct ionic co-crystals urea fertilizers provide different outcomes in this study. Figure. 4.4-11. depicts all of the ANR findings.

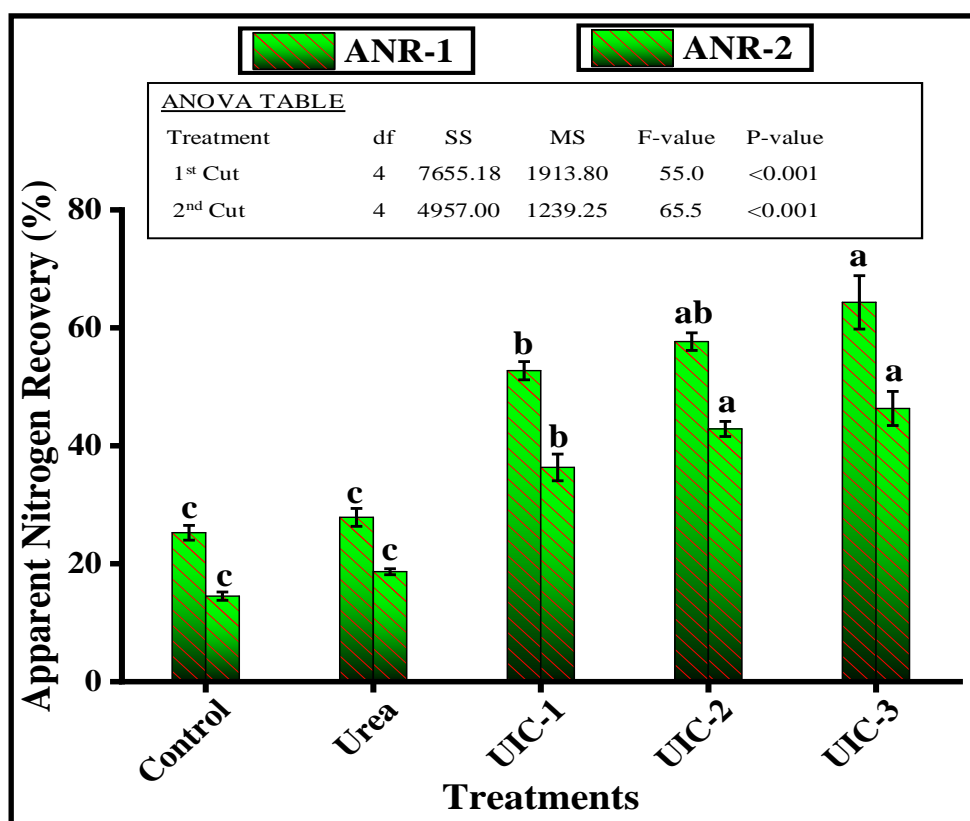


Figure 4.4- 11. Apparent Nitrogen Recovery After The Application Of Urea & Urea Ionic Co-Crystals.

#### 4.5 Plants Growth

The growth of spinach plants during the whole period (0 to 65 days) during both the harvestings are shown as following.





**Day-1 (Sowing)**



**Day-7 Of Sowing**



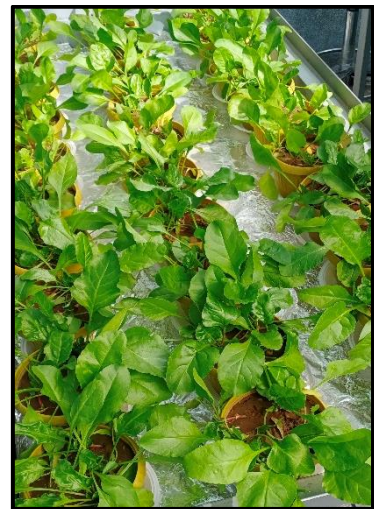
**Day-15 Of Sowing**



**Day-22 Of Sowing**



**Day-29 Of Sowing**



**Day-35 Of Sowing**



**Day-35 (1<sup>st</sup> Harvesting)**



**Day-7 Of 1<sup>st</sup> Harvest**



**Day-15 Of 1<sup>st</sup> Harvest**



**Day-22 Of 1<sup>st</sup> Harvest**



**Day-29 Of 1<sup>st</sup> Harvest**



**Day-65 (2<sup>nd</sup> Harvesting)**

Figure 4.4- 12. Plants Growth.



# Chapter 5

## Release Kinetics

### 5.1 Urea Release Kinetics

The best models for studying the release kinetics of urea and urea ionic co-crystals were chosen in this study. UV spectroscopy was used to investigate the water dissolution rates of urea and ionic co-crystals, and the conclusions were collated to the estimated imitation results [114]. The findings in terms of urea concentration vs time was obtained using a water dissolution experiment. The urea concentration vs. time data was initially translated to release of urea in constituents as indicated in Table. 5.1. and after that put on to the Sinclair and Peppas's formula, modified hyperbola formula, modified Schwartz formula, and Schwartz and Sinclair formula.

Table 5. 1. Fractional Urea Release at 25 °C, Fractional Urea Release Vs. Time. [114]

Sample Name	Fractional Urea Release								
	Time (min)								
	0	3	6	9	12	15	30	60	120
Urea	0	0.426	0.501	0.561	0.592	0.760	1	1	1
UIC-1	0	0.320	0.372	0.389	0.424	0.449	0.488	0.542	0.620
UIC-2	0	0.360	0.368	0.376	0.395	0.455	0.497	0.619	0.745
UIC-3	0	0.335	0.379	0.391	0.409	0.416	0.453	0.474	0.582

### 5.2 Sinclair and Peppas's Model

To estimate the release rate from spherical dimensions, Sinclair and Peppas's Model is usually applied as shown in Table. 5.2. This can accommodate ionic co-crystals, such as urea, which are crystals. This model explains the phenomenon behind the dynamics that control nutrient release [115]. The model's equation can be written as:

$$Q_t = Kt^n \dots\dots (23)$$

The Power Equation is another name for the aforementioned formula.

Where, **K** and **n** are power equation constants.



Table 5. 2. Release Kinetics Data At 25 °C: Sinclair And Peppas's Model. [115]

Model Equation	Sample Name	Adjusted R Square	Value Of "K"	Value Of "n"	Reduced Chi-Square
$Q_t = Kt^n$	Urea	0.80366	0.368	0.232	0.012
	UIC-1	0.99124	0.272	0.172	0.000083
	UIC-2	0.95371	0.239	0.232	0.00090
	UIC-3	0.94539	0.288	0.138	0.00031

### 5.3 Modified Hyperbola Formula

Modified hyperbola formula, described by the following kind, and results are shown in Table. 5.3.

$$Q_t = \frac{at}{1+bt} \dots\dots\dots (24)$$

Small time values reflected first order kinetics, whilst the experiment time progressed, the kinetics approached zero order.

Table 5. 3. Release Kinetics Data At 25 °C: Modified Hyperbola Formula. [115]

Model Equation	Sample Name	Adjusted R Square	Value Of "a"	Value Of "b"	Reduced Chi-Square
$Q_t = \frac{at}{1+bt}$	Urea	0.26085	0.554	-0.0041	0.082
	UIC-1	0.30262	0.344	-0.0040	0.022
	UIC-2	0.46657	0.350	-0.0046	0.022
	UIC-3	0.26665	0.330	-0.0038	0.019

### 5.4 Schwartz and Sinclair Model

The release of coated urea can be studied using this model [116]. Schwartz and Sinclair Formula exemplified by given methods and results are shown in Table. 5.4.

$$Q_t = (1 - e^{-bt}) \dots\dots\dots (25)$$

Table 5. 4. Release Kinetics Data At 25 °C: Schwartz and Sinclair Model. [116]

Model Equation	Sample Name	Adjusted R Square	Value Of "b"	Reduced Chi-Square
$Q_t = (1 - e^{-bt})$	Urea	0.94864	0.101	0.0057
	UIC-1	0.46628	0.027	0.0452
	UIC-2	0.22898	0.031	0.0325
	UIC-3	1.05783	0.020	0.0524

### 5.5 Modified Schwartz Formula

Illustrated as under is the Modified Schwartz formula with the following form and results are shown in Table. 5.5.

$$Q_t = a (1 - e^{-bt}) \dots\dots (26)$$

The emancipation of nutrients from the urea ionic co-crystals is explicated by the first-order kinetics when matrices were formed.

In all aforementioned relations,  $Q_t$  is the fractional urea release at time t, whereas a and b are release constants.

Table 5. 5. Release Kinetics Data At 25 °C: Modified Schwartz Formula. [116]

Model Equation	Sample Name	Adjusted R Square	Value Of "a"	Value Of "b"	Reduced Chi-Square
$Q_t = a(1 - e^{-bt})$	Urea	0.9413	0.999	0.101	0.0065
	UIC-1	0.8832	0.524	0.195	0.0036
	UIC-2	0.7629	0.612	0.121	0.010
	UIC-3	0.8710	0.464	0.320	0.0033

The results of the aforementioned four equations' fitting are shown in Tables. 5.2 - 5.5 respectively. It is depicted in Table. 5.5, the disclosed data has the best match when compared to the other equations. When compared to the other three equations, the results obtained after fitting are the best. The correlation constants values are extremely precise, far patronizing to Sinclair and Peppas's Model, Modified Hyperbola

Formula, and Schwartz and Sinclair Formula. The assertion may be given that the Modified Schwarz and Sinclair formula used in this study is an exceptional representation of nutrient release from ionic co-crystals urea.

## Conclusions

The chief research objectives behind this investigation analysis were to synthesize control release urea fertilizer along with the identification of the best urea ionic co-crystals combination. All combinations were screened and examined using various techniques in which nitrogen was used as plant nutrients along with nutrient phosphorus and potassium for enhancement of soil fertility. Amalgamation of organic and inorganic progenitors in ionic co-crystals, such as ZnKU along with Urea Nitrate, and Urea Phosphate were used as compacting materials. All the combinations were applied to UV VIS Spectroscopy examination to check the emancipation of Urea-N from urea ionic c-crystals in comparison with uncoated urea. All urea ionic co-crystals showed the best results for Urea-N release in terms of control release characteristics. Spectroscopy and Crushing strength analysis results revealed that the addition of compacting materials with urea retarded the release rate in water more as compared to uncompact urea. UIC-2 treatment materials crushing strength was reported as 214.71 N, followed by UIC-3 with 198.36 N. SEM micrograph of UIC-3 showed compacted structure among all combinations.

After the preparation of urea ionic co-crystals pot test experiment conducted using a complete randomized block with six repetitions. Control (untreated) was also kept. Spinach was sown as a test plant. All soil sampling was done at 0 days and after harvesting of spinach twice (35 days and 65 days).

Plant analysis was conducted after the harvesting of spinach plants. There is no noticeable increase in soil pH. Soil EC enhances after UIC's fertilizer used. Maximum EC was observed in UIC-1 (0.81 dS/m) and the minimum was observed in UIC-2 (0.67 dS/m). TOC value is highest in UIC-3 (8.91 Mg/hac) and less value was shown by UC (7.34 Mg/hac). OM content is highest in UIC-3 (0.77%) and less value was shown by UC (0.63%). Results show that MBC and MBN from UIC-3 treatment are maximum of 175 mg/kg and 93.38 mg/kg respectively, followed by UIC-2 treatment of 147.98 mg/kg and 85.61 mg/kg respectively. MBP and MBK results revealed that treatment UIC-3 shows maximum contents of 23.96 mg/kg and 63.33 mg/kg respectively, followed by UIC-2 treatment of 19 mg/kg and 57.75 mg/kg respectively. In mineral nitrogen UIC-3 and UC treatment represent highest and lowest value of both Ammonium-N and Nitrate-N sequentially in soil as well as leachate.

Observing the plant analysis, it is observed that in UIC treatment has maximum plant height (23.15 cm and 13.26 cm), plant diameter (2.68 mm and 1.60 mm), leaf area (34601 cm/m<sup>2</sup> and 20623 cm/m<sup>2</sup>), and leaf area index (3.46 m/m<sup>2</sup> and 2.06 m/m<sup>2</sup>) was recorded after both harvestings respectively. Moreover, UIC-3 treatment gave the best result in terms of spinach fresh mass, dry mass yield and nitrogen uptake after both harvestings. From all release rates of fertilizer in water and pot test experiment on plant concluded that UIC-3 fertilizer gives the best result followed by UIC-2 fertilizer.

## Recommendations

This investigation study supplied a prominent way to review all other features and properties associated with the development of indigenous control release UIC's fertilizer

are as follows:

- Release kinetics can also be carried out in soil with specified moisture content to check better mechanisms.
- Release kinetics can be performed at a different temperature to check the effect of temperature on the release rate.
- Excessive pot tests to be conducted on various plants with different soils to check the impact of urea ionic co-crystals on plant growth.
- We can demonstrate the application of mechanochemistry to conduct the synthesis of other secondary nutrients-urea ionic co-crystals including their nitrates, sulfates and phosphates, in high yields by stoichiometric reactions between abundant low solubility minerals, such as oxides, carbonates and hydroxides and solid urea inorganic acids for better results.
- Use compounds of some other secondary nutrients (Ca, Mg etc) or micronutrients (zinc, iron, etc.) as compacting materials to test the changes in release patterns.
- Combination of environment friendly organic and inorganic precursors that are degradable and does not affect the soil composition should be used.

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