Environmentally Friendly Slow-Release Urea Fertilizer Based on Iron and Geo-Polymer Coating for Sustainable Nutrient Release

By

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2023

Environmentally Friendly Slow-Release Urea Fertilizer Based on Iron and Geo-Polymer Coating for Sustainable Nutrient Release

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MS in Chemical Engineering

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May, 2023

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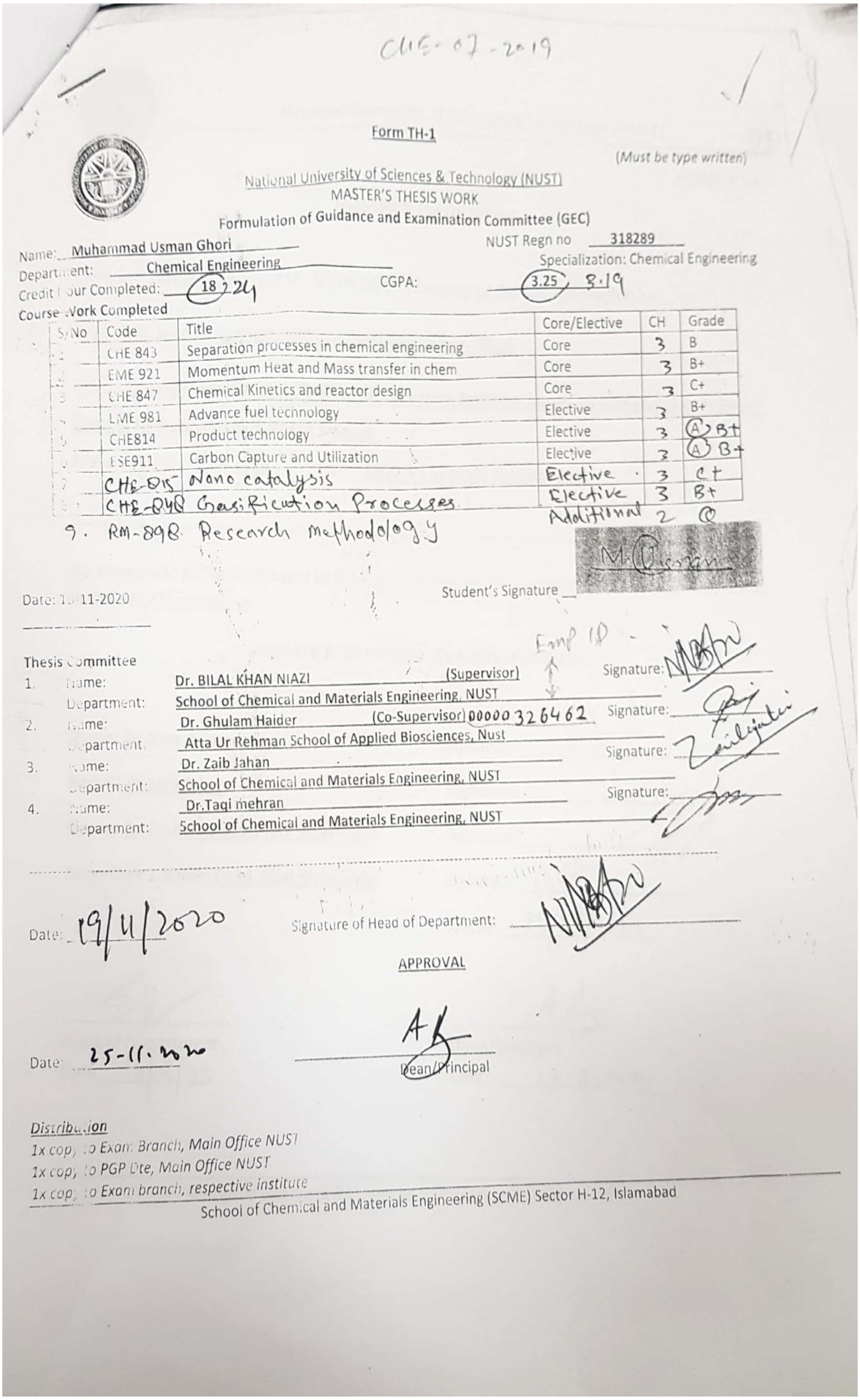

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CGPA: 3.25, 3.19

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S/No	Code	Title	Core/Elective	CH	Grade
1	CHE 843	Separation processes in chemical engineering	Core	3	B
2	EME 921	Momentum Heat and Mass transfer in chem	Core	3	B+
3	CHE 847	Chemical Kinetics and reactor design	Core	3	C+
4	EME 981	Advance fuel technology	Elective	3	B+
5	CHE814	Product technology	Elective	3	A, B+
6	ESE911	Carbon Capture and Utilization	Elective	3	A, B+
7	CHE-815	Nano catalysis	Elective	3	C+
8	CHE-848	Gasification Processes	Elective	3	B+
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Dedication

By the grace of Almighty Allah, who is the most Beneficent and the most merciful.

This research is dedicated to my parents, who have always been my source of guidance and support.

To my supervisor who shared his knowledge, gave advice, and encouraged me to fulfill my tasks.

And to all my fellows, with whom I worked and shared good memories.

Acknowledgements

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.

I am immensely grateful to my research supervisor Dr. Muhammad Bilal Khan Niazi, (H.O.D Research - SCME NUST), for providing me with all of the necessary research resources, for his unwavering support throughout my MS studies and research, as well as his encouragement, patience, excitement, and vast knowledge. His advice was invaluable during the research and writing of this thesis. I could not have asked for a greater counsellor and mentor.

I'd also like to express my gratitude to Professor Dr. Ghulam Haider (ASAB-NUST) for offering a research-oriented platform to productively utilize my knowledge and skills in completion of the project and for providing me with all of the essential research resources.

Apart from my advisor, I'd want to convey my gratefulness to the rest of my research panel including Co-Supervisor Dr. Taqi Mehran, Dr. Zaib Jahan, and Dr. Muhammad Qasim Hayat for their support, intelligent comments, and difficult questions to improve my research.

I'd also like to thank all SCME and ASAB lab staff members for their assistance in the lab and for their positive attitude.

Muhammad Usman Gauri

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. Encapsulation of Fertilizers in Geopolymeric coatings is the method to reduce loses of the important nutrients of the Fertilizers and lowers the environmental pollution by reducing contamination of water, air etc. Coatings of Iron with Poly-acrylic acid blends are used to encapsulate the Urea granules in Fluidized bed coater. Moreover, different methods including SEM, XRD, UV-Vis Spectroscopy, FTIR, Soil 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 fertilizer 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.

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Chapter 1

Introduction

1.1 Background

Over the previous century, expanded fertilizer, water, and pesticide treatments, combined with modern technologies, have led to huge advancements in modern agriculture. Crop yields per unit land area has gradually upgrades, 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 tons in 2000-2001 to 185 million tons in 2014- 2015, with global market expected to exceed 200 million tons in 2022-23 [8]. The use of normal industrial urea fertilizer has several drawbacks, including a number of environmental concerns. This is indeed an issue that is being debated 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 N 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 2 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 fertilizer, 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 groups.

The 3 elements i-e., C, H, O 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. [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 3 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]. Essential Plant Nutrients. [16] Essential Plant Nutrients (16) Mineral (03) Non-Mineral (13) Macronutrients (06) Micronutrients (07) Primary (03) Secondary (03) Hydrogen Nitrogen Calcium Boron Oxygen Phosphorus Magnesium Copper Carbon Potassium Sulfur Iron Chlorine Manganese Molybdenum Zinc 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. 4 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 Non-Mineral Elements Carbon C Are over 90% of total dry matter of plant CO_2(g) Building Blocks Of Hydrogen H H_2O(l) & H+ Macromolecules. Oxygen O H_2O(l) & O_2 Mineral Elements Major Nutrients Nitrogen N 100 NH_4^+ & NO_3^- Proteins, Amino Acids Phosphorus P 6 HPO_4^+ & $H_2PO_4^-$ Nucleic Acids, ATP Potassium K 25 K^+ Catalyst, Ion Transport Secondary Nutrients Calcium Ca 12.5

Ca^{2+} Cell Wall Constituent Magnesium Mg 8 Mg^{2+} Part Of Chlorophyll Sulfur S 3 SO_4^{2-} Amino Acids Micronutrients Iron Fe 0.2 Fe^{2+} & Fe^{3+} Chlorophyll Production Manganese Mn 0.1 Mn^{2+} Activates Enzymes Zinc Zn 0.03 Zn^{2+} Activates Enzymes Copper Cu 0.01 Cu^{2+} Constituent Of Enzymes Boron B 0.2 $B(OH_3)$ (boric acid) Cell Wall Constituent Molybdenum Mo 0.0001 MoO_4^{2-} N Fixation Chlorine Cl 0.3 Cl^- Photosynthesis Reactions 5

1.4 Nutrients Loss

Plants can easily obtain N from urea. The rate of N 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

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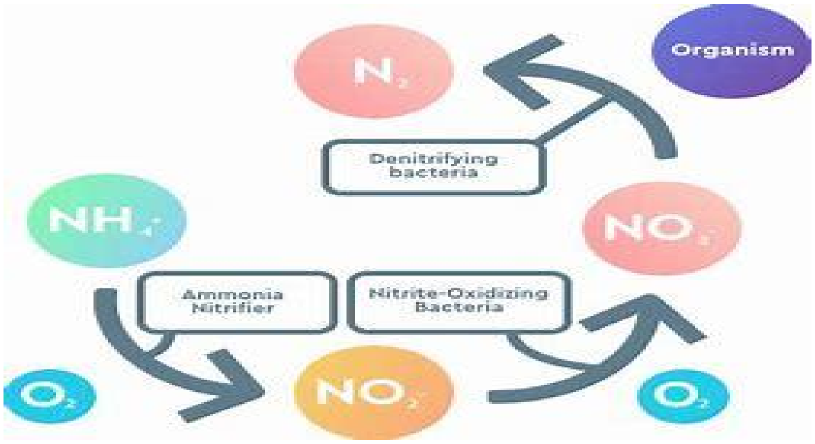


Figure 1 Reaction Route of Nitrification and Denitrification Processes [21]

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 fertilizer developed from NH_3 and CO_2, with an estimated yearly production of 226 million tonnes in 2021 [26]. NH_3 is formed by hydrogenating N_2 with H_2 generated from natural gas, a process that utilizes approximately 1% of worldwide energy and ~4% of total natural gas production [27]. According to Figure 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 1015 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. [2]

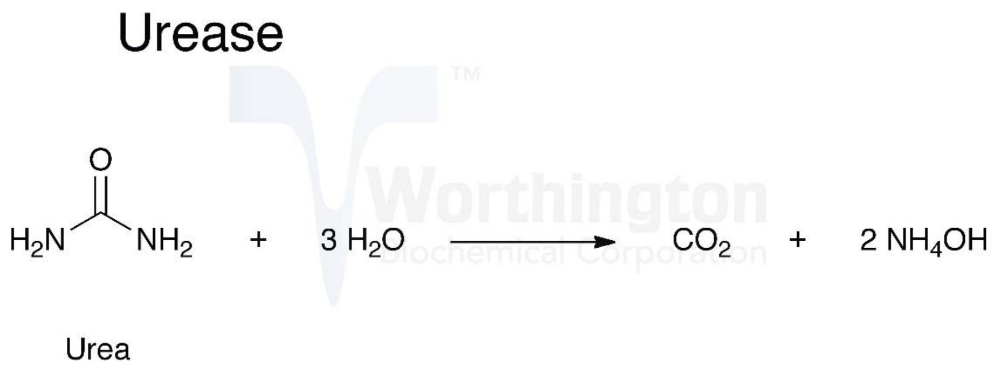


Figure 2 Overall Hydrolysis of Urea

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 Figure 3) 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 NOx, NH_3, and N_2O (a GHG about 300 times the heat-trapping capability of CO_2), [35] as shown in Figure 3.

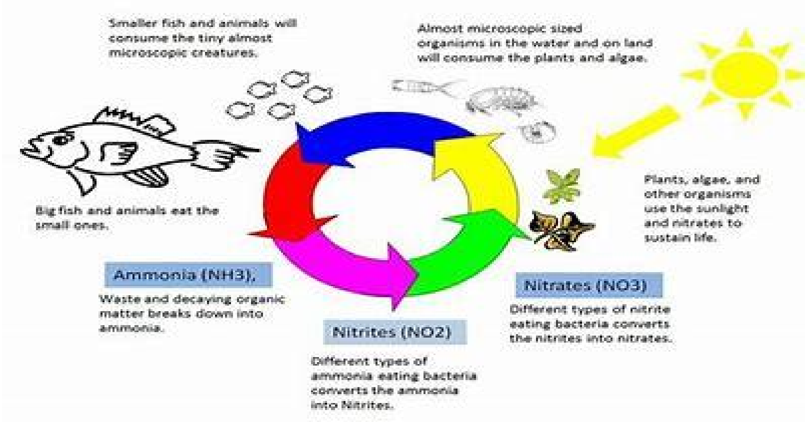


Figure 3 Nitrogen Cycle

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 NO_3 to the diatomic nitrogen gas N_2. Leaching is also classified as permanent losses when NO_3 is moved downward from the plant's root sector. Volatilization losses from the earth's surface associated with 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.

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

Slow or controlled 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 fertilizer 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 the 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 micronutrients (Zn, Cl) to the plants. Vitally, 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 % [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 reduces NH3 losses [44]. 9 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.). Ionic Co-crystals Of Urea with Improved Urease Inhibition. [44].

1.8 Prons 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 the 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 is also boosted by the controlled delivery of N from the described urea synthesis approach. The 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 12 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 N 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.

1.9 Cons 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 that 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].

1.10 Statement of Problem

Fertilizers are backbone of agrochemical industry of any country. They provide necessary nutrients to the soil that are essential for plant growth, but use of conventional Fertilizers may lead to concentration levels that re too much high for effective action. High concentration nutrients may produce undesirable side effects either in the fields and plants or in surrounding environment which may cause crop damage or environment pollution. Slow release Fertilizers method is used to reduce the nutrient loses effectively.

1.11 Purpose of Study

Recent statistics shows a prevalence of around 45% of Iron deficiency anemia in Pakistan, which is quite high realizing the failure of public health measures to control it. According to EMRO WHO statistics, it has been found that more than one-fifth of women in Pakistan suffer from anemia. To compensate this deficiency of Iron in human beings our research is based on Iron nanoparticles.

Moreover International imports of fertilizer will be countdown by enhancing its efficiency. Even a 10% increase in its efficiency would mean that there is no requirement of imported urea. Due to urea fertilizer shortages in Pakistan, provides a motivation for young researchers like me to carry out research indicate indigenous slow release of urea by coating with different materials saving fertilizer and energy. This is the first ever project in the history of Pakistan that will look in to technological bottlenecks of urea fertilizer release rate in order to enhance its efficiency.

1.12 Contribution of Study

The objective is as follow

- Synthesis and characterization of Iron Nanoparticles
- Development and characterization of iron nanoparticles and geopolymer based slow release coated Urea fertilizer using SEM, XRD, FTIR, and UV-VIS Spectroscopy
- Study the release rate of nitrogen from coated fertilizer using Kjeldahl apparatus
- Study the release rate of Iron from iron coated urea fertilizer

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 $ZnCl_2$ 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 customizations 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. $ZnCl_2$.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 $ZnCl_2$ 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°C. 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°C). 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.

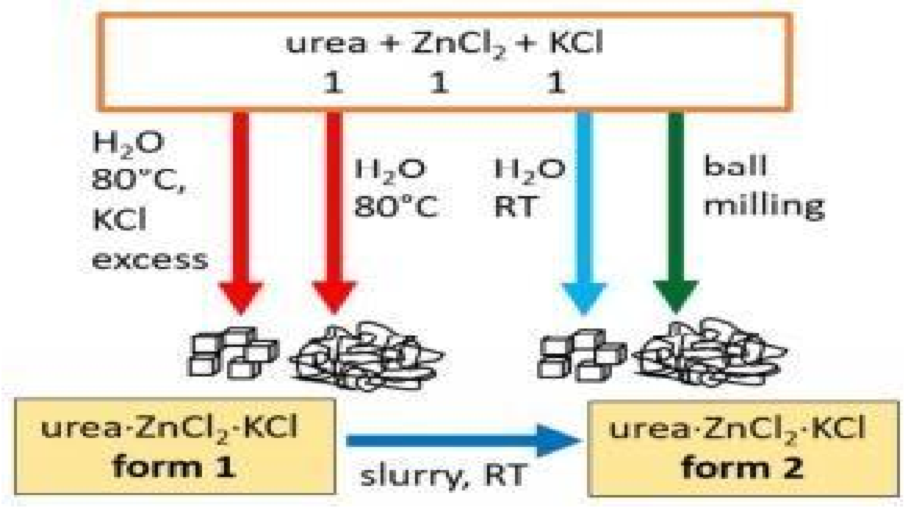


Figure 4 ZnKU Forms 1 & 2 Obtained By Reacting Urea, ZnCl2 And KCl In 1:1:1 Stoichiometric Ratio.[25]

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 be them in this conveyance. In order to raise the inhibition/fertilization duality, the mixture of ZnKU and urea is provided in an 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 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 NH_3 resulting from ionic cocrystal $CaSO_4 \cdot 4CO(NH_2)_2$ 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 H_2O 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^{o}C 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 manipulation, 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 69 and estimation of the comparable reaction wavering.

2.2.2 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 drywell gypsum waste which is extensively plentiful. Distinctive reactive characteristics are owned by the resulting $CaSO_4$. 4urea 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 ℃. An exertion in which urea ($CO(NH_2)_2$, 99.5 %) and calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$, 99.3 %) powders were utilized together with marketable gypsum drywall powder was executed by Karolina Barčauskaitė et al. in 2020. In combination with urea- $CaSO_4{\cdot}2H_2O$ 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 ± 5 °C for one whole day.

The mechanochemical coalescence of CaSO4.4urea 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 CaSO4.4urea 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 abase 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 form 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 $CaSO_4.2H_2O$- 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 CO_2 corresponding per kg N riveted for the support of this evidence. Contrary to this, ~0.01 kW h/kg is needed by a conventional industrial ball-mill which is expressed as 0.005 kg CO_2 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.

2.3 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 pharmaceutics, 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.

2.3.1 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 congregation, 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).
- Hydroxamtes.

- 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. Inquests and experiential trial have also been conducted with N-(2-nitrophenyl) phosphoric acid triamide (2-NPT) and ammonium thiosulphate (ATS). 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 availablewhich 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 inhibitor.

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 the 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 include Urea (extra pure), along with compacting materials iron nanoparticles, acrylic acid, Polyvinyl acetate, Deionized water, Iron chloride (FeCl3), Iron hydroxide (Fe_3O_4), Nitric Acid (HNO3) were imported from Sigma-Aldrich along with Urea Prills that was imported from MACKLIN. The, Polyvinyl acetate includes Polyvinyl alcohol and amine. The binder includes is starch, paraffin liquid, and Polyethylene glycol which are imported by the local market of Islamabad.

3.2 Preparation method of urea coating

A total of 10 g of starch mixed with 100 ml of deionized water and stir with 30 minutes at 80^oC. After that appropriate quantities of Polyvinyl acetate and iron oxide nanoparticles are added for 2 hrs at 80^oC (urea nitrate or urea phosphate) and urea mixture with the corresponding molar ratios. Table. 1. shows the combination of compacting materials used to create urea ionic co-crystals

Table 1 Synthesis of Urea Coating

Sample Name	**Treatment**	**Name of materials**	**Molar ratio**
Urea	Treatment 1	Starch Binds	10
		PVA Geopolymer	10
		Iron Nanoparticles	-
Urea	Treatment 2	Starch Binds	10
		PVA Geopolymer	-
		Iron Nanoparticles	10
Urea	Treatment 3	Starch Binds	10
		PVA Geopolymer	5
		Iron Nanoparticles	5

3.3 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^{-1}. A Universal testing machine (AGX Plus) was used to conduct crushing tests on urea crystals. On X-ray diffraction equipment, simple and ionic co-crystals of urea were studied using a scan angle extend over from 10 to 90^{o}.

3.3.1 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.

3.3.1 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.

3.3.2 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 cm^{-1}, the urea crystals were squashsed 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.

3.3.3 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 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].

3.3.4 X-Ray Diffraction (XRD)

X-ray diffraction (XRD), of uncompacted 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 10º to 90º. Step size and step time were taken as 0.4 degrees & 1 second respectively. Radiation used for depiction was of Cu K α-1 [85].

3.4 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 utilzed to analyze the release rate and effectiveness of simple and ionic co-crystals urea.

3.4.1 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 (20 ppm, 40 ppm, 60 ppm, 80 ppm, and 1000 ppm). The absorbance of these reference solution was measured by a UV-Visible Spectrophotometer, as indicated in **Table. 2** Afterwards, as illustrated in **Figure 5,** 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.

3.4.1.1. 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.

Urea(ppm) = (Absorbance − Y. Intercept) ÷ (Slope from calibration curve) … (1)

Efficiency (%) = $C_U - C_{UI} / C_U \times 100$.. (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 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 = 0.001

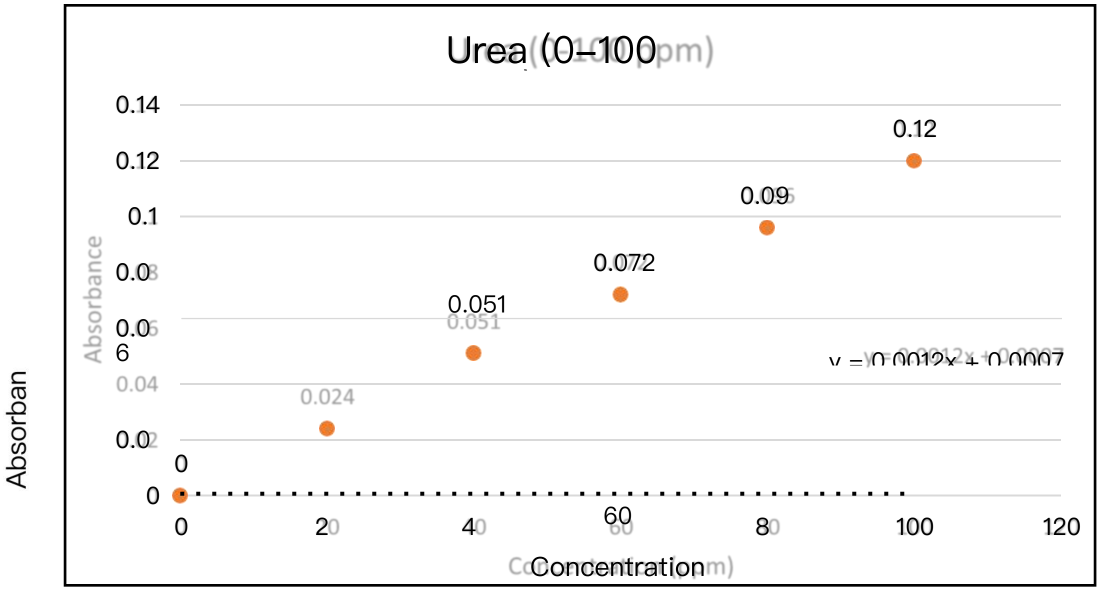


Figure 5 Standard Curve of Urea Concentration And Absorbance [82]

3.5 Pot Experimentation

3.5.1 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.

3.5.2 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^2. 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.

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.

3.5.3 Treatments

T1	**Control**
T2	**UC Urea**
T3	**UIC-1 Urea**
T4	**UIC-2 Urea**
T5	**UIC-3 Urea**

3.6 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 ($\mathbf{NO}^{-}$)$_3$, Ammonium-Nitrogen ($\mathbf{NH}^{+}$)$_4$ [60].

3.6.1 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].

$$\textbf{Soil Moisture} = \frac{\boldsymbol{Wet\ soil - Dry\ Soil}}{\boldsymbol{Wet\ Soil}} \qquad \textbf{(3)}$$

$$\textbf{Moisture Factor} = \frac{\boldsymbol{100 + \%soil\ mositure}}{\boldsymbol{Dry\ Soil}} \qquad \textbf{(4)}$$

3.6.2 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]:

$$100\% \text{ water holding Capacity} = \frac{W1 - W2}{W2} \times 100 \qquad (5)$$

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 every day. And kept the water loss constant throughout the trial.

3.6.3 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].

3.6.4 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].

3.6.5 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_2SO_4 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].

% Oxidixable Oraganic Carbon =[VB-VS]x0.3x M /Wt (6)

% Total Organic Carbon = 1.334 × (% Oxidizable Organic Carbon) …. (7)

% Organic Matter = 1.724 × (% Total Organic Carbon) …… (8)

Where,

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

V_B = Volume of ferrous ammonium sulphate solution required to titrate the blank (ml)

V_S = Volume of ferrous ammonium sulphate solution required to titrate the sample (ml)

W_t = Weight of air-dry soil (g)

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

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

V1 = Volume of soil extract used for digestion (ml)

V2 = Volume of soil digest used for distillation (ml)

14.01 = Atomic weight of N

ϴ = Weight of water (g) per oven-dry soil

3.3.1 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 $NaHCO_3$ solution [93] and agitate the solution constantly for 2 h in a wobbling round inoculator. The filtration of solution was done using Whatman number 42 filter paper. Add 5 g soil and mix it with 25 ml of 0.5 M $NaHCO_3$ 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 color developing solution. The optical density of phosphorus was measured using a spectrophotometer (Cecil, CE2021, 2000 configuration) [87, 94-96].

Table 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.

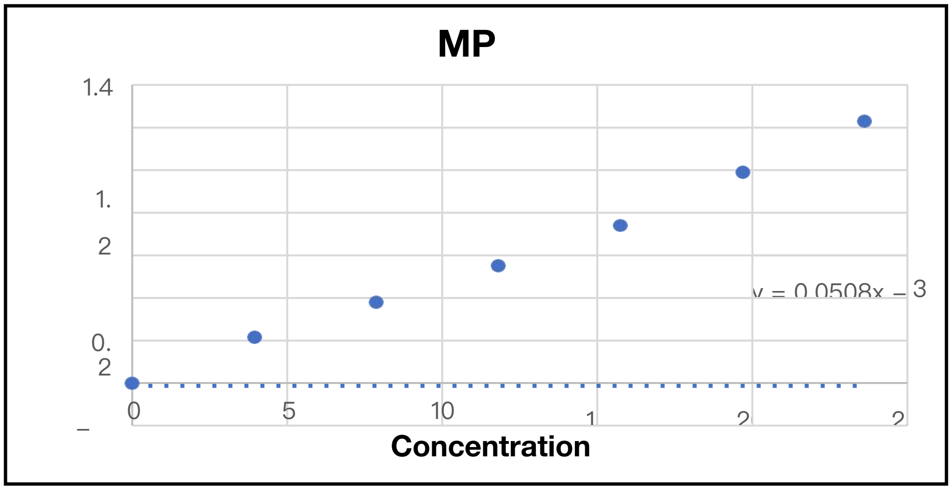


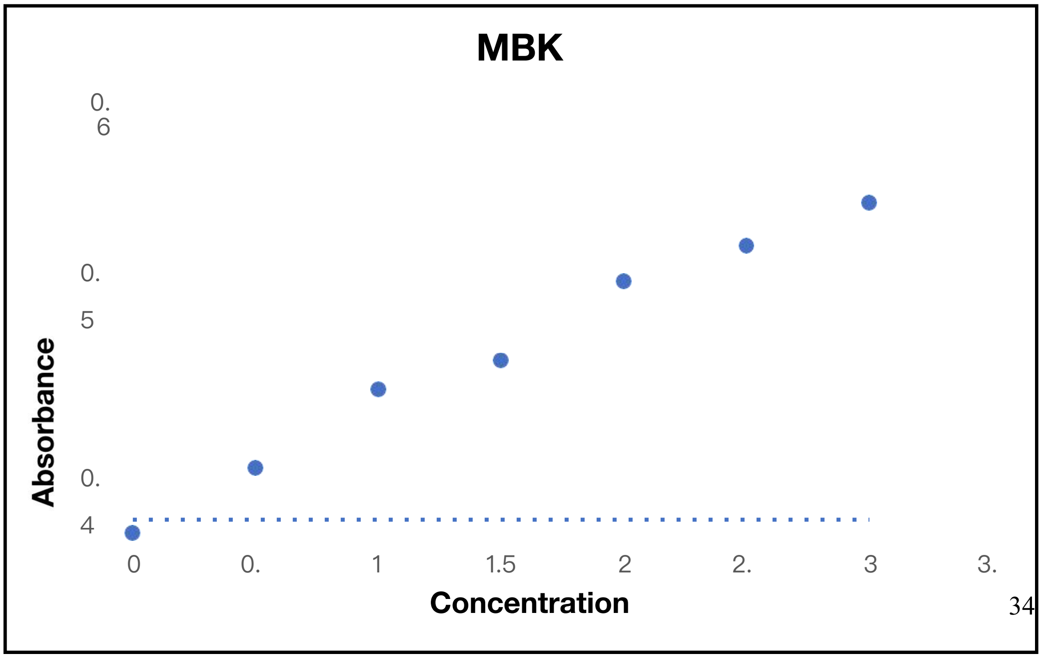
Figure 6 Standard Curve of MBP Concentration and Absorbance.

3.3.2 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 inoculation. The filtration of solution was done with the help of Whatman number 42 filter paper. Add 5 g soil a

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 number 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].



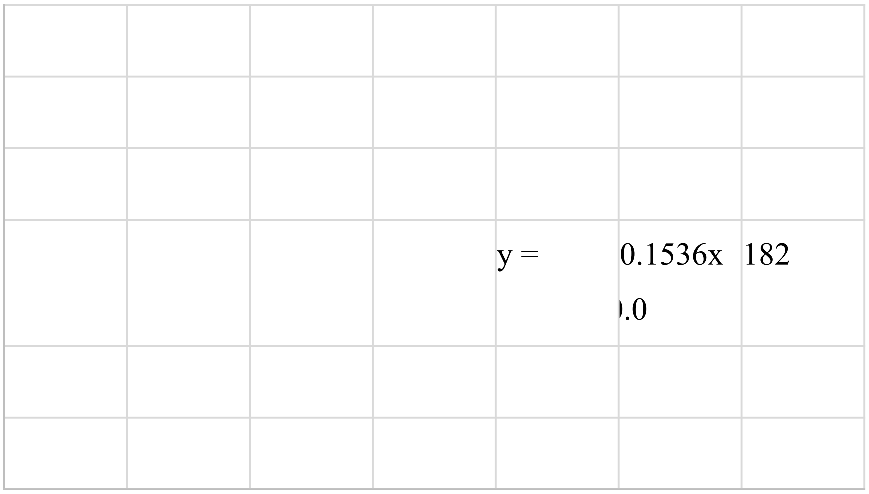


Figure 7 Standard Curve of MBK Concentration And Absorbance.

3.3.3 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.

3.3.1.1 Nitrate Nitrogen ($NO^{-}_{3} - N$)

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 $NO3^{-}$ - N L^{-1}. Now absorbance was noted using a microplate reader, as indicated in **Table 4.** Afterwards, as illustrated in **Figure 8.,** a standard curve was produced by drawing a plot between known nitrate concentrations and absorbance. The test procedure is given below.

Test Procedure

First of all extraction solution of 0.5M K_2SO_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]:

Vanadium Chloride (VCl_3) i.e. (0.8 g of VCl_3 in 50 ml of concentrated HCl).

Sulfanilamide solution i.e. (2 g Sulfanilamide bring to 100 ml volume with 5% (v/v) HCl. 0.1% (w/v) NEDD (N-(1-napthyl) 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 VCl_3: 10 ml Sulfanilamide: 10 ml NEDD). After that 100 µl of premix solution was added to 100 µl 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].

Nitrate-Nitrogen (mgL^{-1}) = (Absorbance − Y. Intercept) ÷ (Slope from calibration curve)...(13)

Table 4 (NO_3^{-1} − 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.

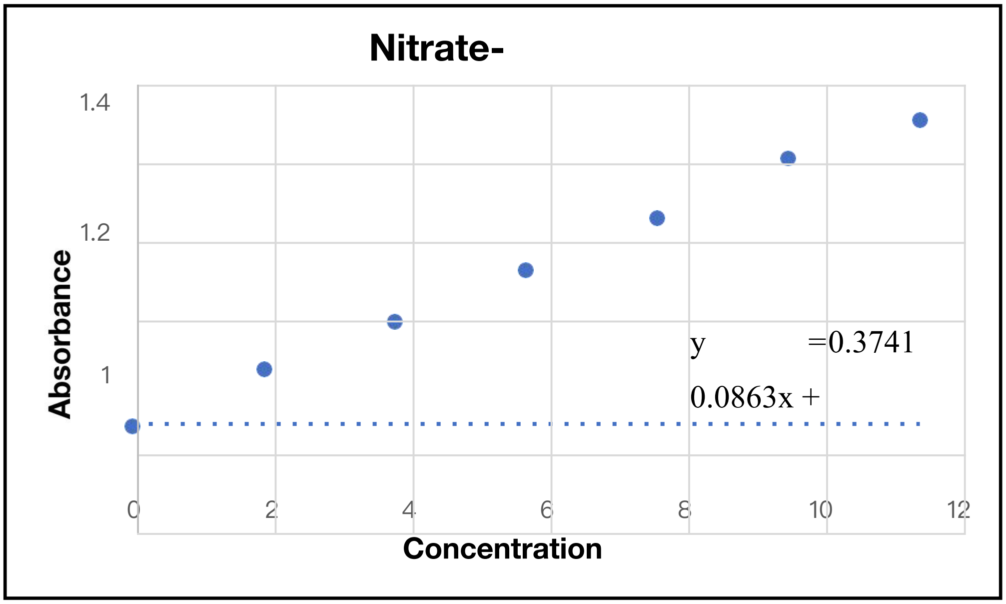


Figure 8 Standard Curve of Nitrate-Nitrogen Concentration and Absorbance. [100, 101]

3.6.8.2 Ammonium-Nitrogen ($NH_4^+ - N$)

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 NH_4^+ - N L^{-1}. Now absorbance was noted using a microplate reader, as indicated in **Table. 5.** Afterwards, as illustrated in **Figure.9** a standard curve was produced by drawing a plot between known ammonium concentrations and absorbance. The test procedure is given below.

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 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 cicumvent 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].

Ammonium-Nitrogen (mgL^{-1}) = (Absorbance − Y. Intercept) ÷ (Slope from calibration curve)...(14)

Table 5 ($NH_4^+ - N$) 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

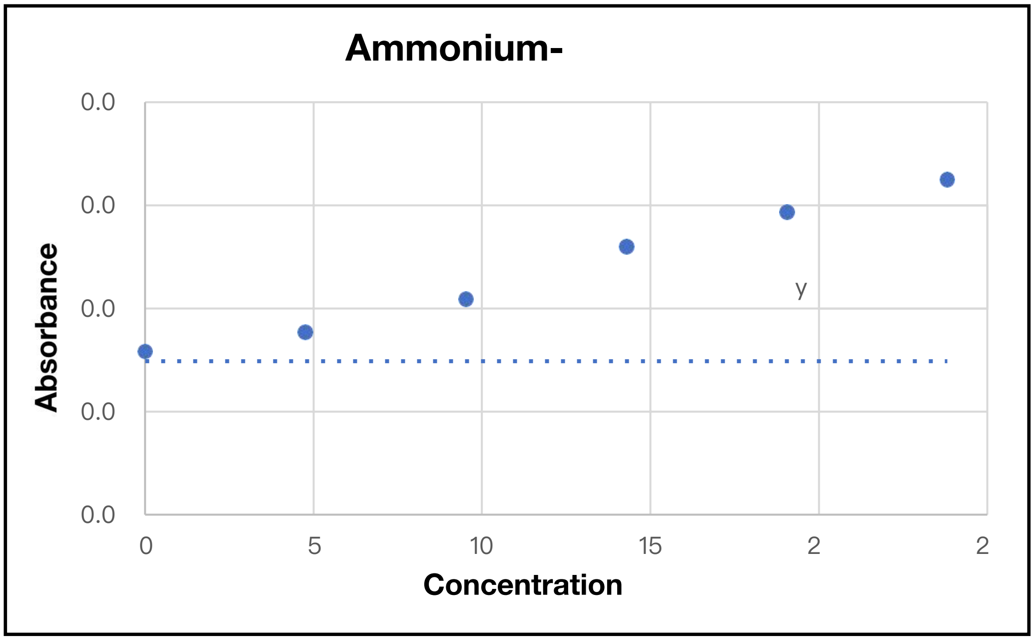


Figure 9 Standard Curve of Ammonium-Nitrogen Concentration And Absorbance *[100, 102]*

3.4 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

3.4.1 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.

3.4.2 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.

3.4.3 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 cm^2.

3.4.4 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.

3.4.5 Dry Weight

Fresh specimens are withered at 70°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.

3.4.6 Chlorophyll Values

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

3.4.6.1 Chlorophyll Values Via SPAD Meter

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

3.4.6.2 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:

$$\mathbf{Chl\ (a) = 12.71 \times (A663) - 2.69 \times (A645) \ldots\ldots. (15)}$$

$$\mathbf{Chl\ (b) = 22.9 \times (A645) - 4.68 \times (A663) \ldots\ldots. (16)}$$

$$\mathbf{Total\ Chlorophyll = 20.02\ (A645) + 8.02\ (A663) \ldots\ldots\ldots (17)}$$

3.8 Nutrient analysis

Digestion

Dried ground material (0.5 g) was taken in digestion tubes and 5 mL of concentrated H_2SO_4 were added to each tube (Wolf, 1982). All the tubes were incubated overnight at room temperature. Then 0.5 mL of H_2O_2 (35%) poured down the sides of the digestion tube, ported the tubes in a digestion block and heated at 350°C until fumes were produced. They were continued to heat for another 30 min. The digestion tubes were removed from the block and cooled and 0.5 mL of H_2O_2 was slowly added and the tubes were placed back into the digestion block. The above step was repeated till the cooled digested material was colorless. The volume of the extract was maintained up to 50 mL in volumetric flasks. The extract was filtered and used for determining nitrogen .

Procedure

Take 5 mL of the above aliquot in Kjeldahl flask, place it on the Kjeldahl ammonia distillation unit, add 5 mL of 40% NaOH. Take 5 mL of boric acid solution in a conical flask with few drops of mixed indicator. When the distillate is approximately 40 mL, stop the distillation. Cool the distillate for few minutes and titrate it with 0.01 *N* standard H_2SO_4 till the solution turns pink. Run a blank for the complete procedure.

Estimate N by the following formula;

N %age = $\underline{(V_2\text{-}V_1) \text{ x } N \text{ x } 0.014 \text{ x } 100}$ W

Where

V_2 = Volume of standard H_2SO_4 required to titrate the sample solution.

V1 = Volume of standard H_2SO_4 required to titrate the blank solution.

N = Normality of H_2SO_4

W = Weight of the sample in g

Chapter 4

Results and discussion

4.1 Analysis of synthesis of iron nanoparticles:

4.1.1 Fourier Transform Infrared radiation.

The FTIR Spectrum of iron particle is done with the help of Pellet KBR and different peaks is observe. The FTIR spectrum of untreated urea was given in the **Figure 10.** At wavelength 3428.1 show the presence of-OH group. At wavelength 2925 cm^{-1}, stretching vibrations are exhibited by urea due to the presence of CH and N-H. At peak 1630 cm^{-1} is a carbonyl (CO) and at the peak of 1428 cm^{-1} is a bending vibration NH and CH stretching vibration of O = C-NH$_2$ [106-108]. C-H overtone stretching vibrations are observed at 1053 cm^{-1}. The peak at 618 cm^{-1} represents the strong stretching vibrations of iron.

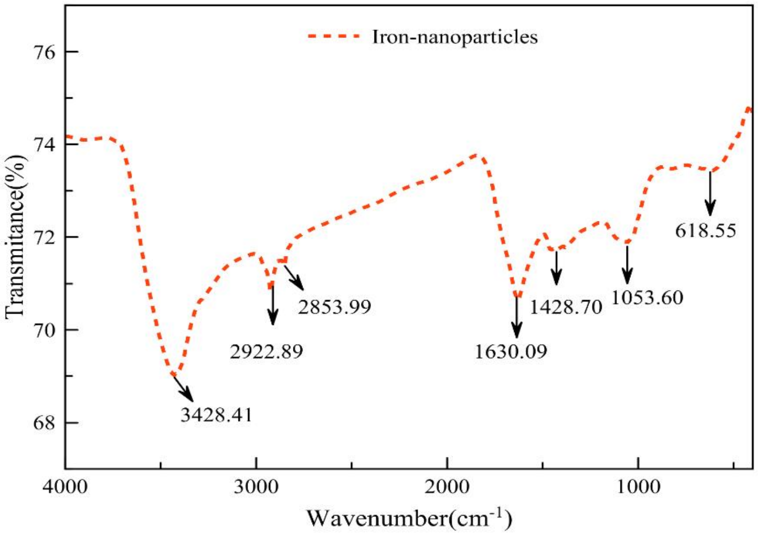


Figure 10 FTIR of Iron Synthesis

4.1.2 Scanning Electron Microscope

The green iron oxide created synthetic ally's surface morphology. Scanning electron microscopy was initially used to study nanoparticles. (SEM). Figure 11 displays the SEM images of the Fe_2O_3 that were taken, which demonstrated the emergence of spherical nanoclusters that include a significant number of smaller nanoparticles that are related to the nanoparticles' agglomeration. The elements that make up the EDS analysis was used to analyse the produced nanoparticles. The outcome shown that the nanoparticles contain approximately 39.37 % of iron.

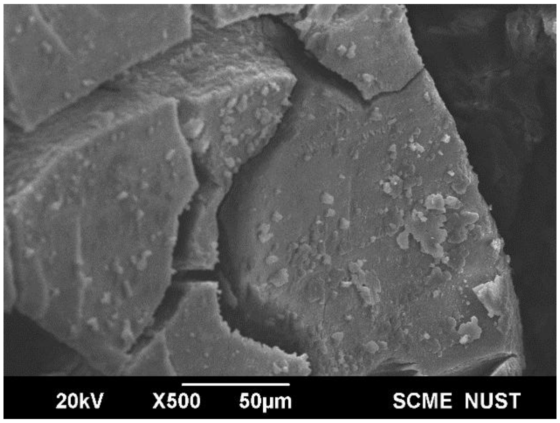


Figure 11 Morphology of iron synthesis

4.1.3 X-ray Diffraction

Iron oxide NPs produced by extract showed diffraction peaks at 24.20, 33.19, 35.68, 40.87, 49.52, 54.10, and 64.00, which were indexed to (012), (104), (110), (113), and correspondingly (440), planes of the rhombohedral hematite phase (024), (116), and (300) (JCPDS 89-0599) Magnetite nanoparticles (Fe_2O_3) (Fig. 12). That is XRD pattern shows no sign of any extra planes, which suggests that the highly pure Fe_2O_3 NPs produced during green synthesis were attained at minimal temperatures.

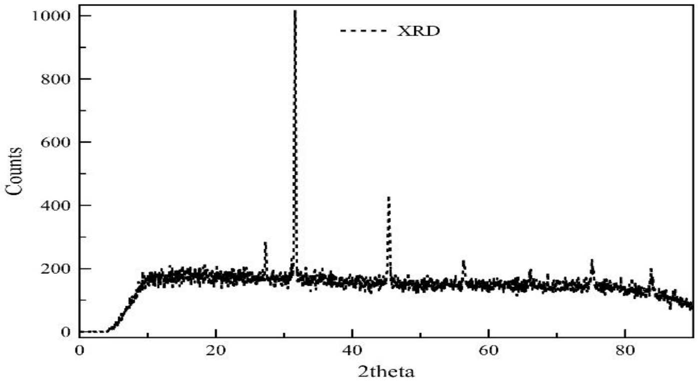


Figure 12 X-ray Diffraction of iron nanoparticles

4.2 Release Rate Analysis of Urea Ionic Co-Crystals

4.2.1 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. 6.**

Table 6. 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

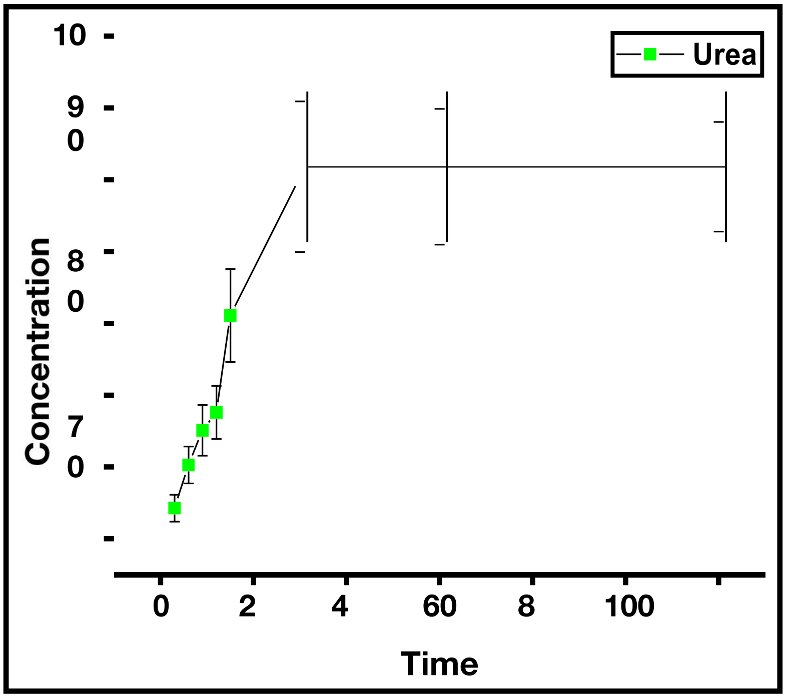


Figure 13 Uncoated Urea Release: Time (min) Vs. Urea Concentration (ppm).

The correlation between untreated urea concentrations (ppm) and time (min) is depicted in **Figure. 13.** 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 reduces the release rate up to 2.01 times, as depicted in **Figure. 14.**

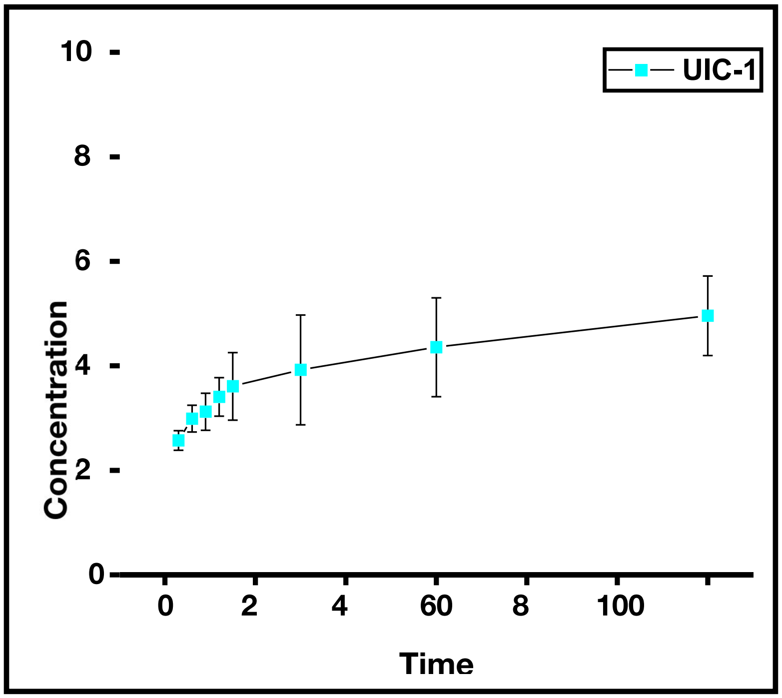


Figure 14 UIC-1 Urea Release: Time (min) Vs. Urea Concentration (ppm).

Figure. 15. 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 slow release and reduce the release rate up to 1.67 times.

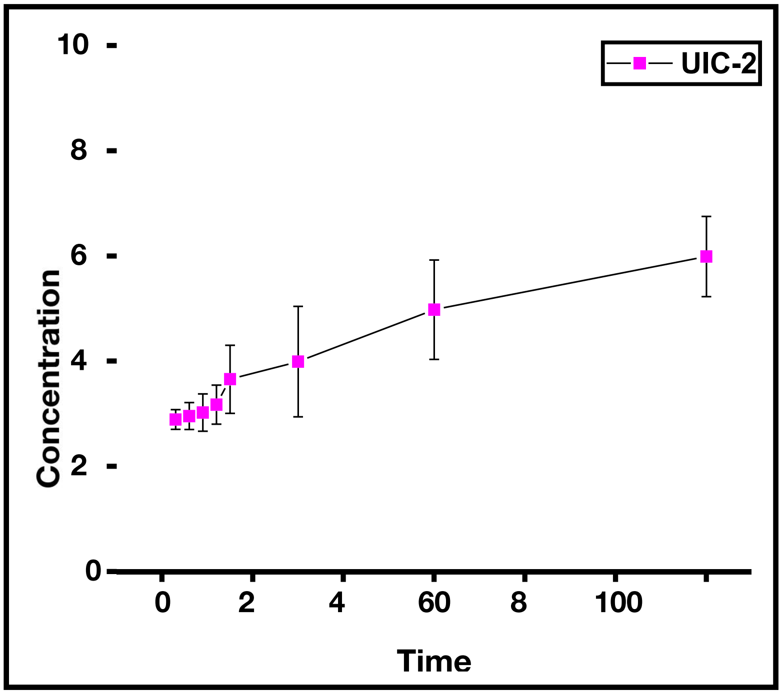


Figure 15 UIC-2 Urea Release: Time (min) Vs. Urea Concentration (ppm).

In contrast, as depicted in **Figure. 16.** 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.

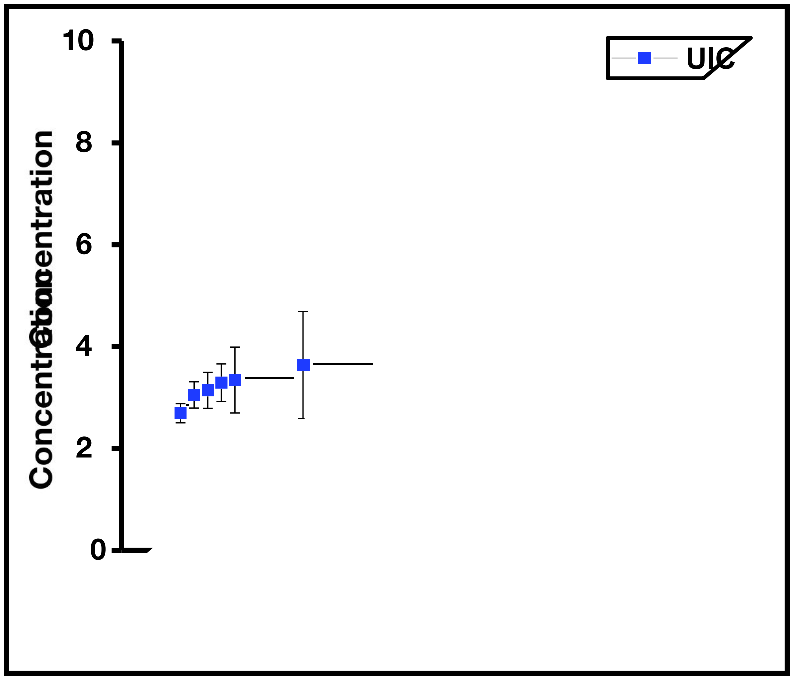


Figure 16 UIC-2 Urea Release: Time (min) Vs. Urea Concentration (ppm).

Table. 7 and **Figure. 17.** 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 7. 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**

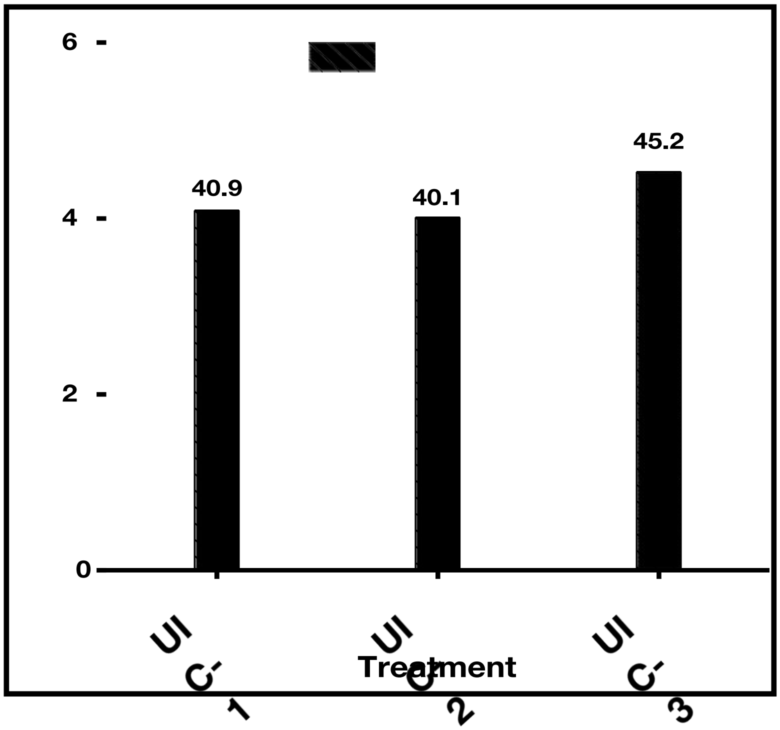


Figure 17 UIC’s Efficiency At 15 Minutes: Samples Vs. Efficiency (%).

4.3 Release Rate Analysis of Urea Ionic Co-Crystals

4.3.1 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. 8.**

Table 8 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

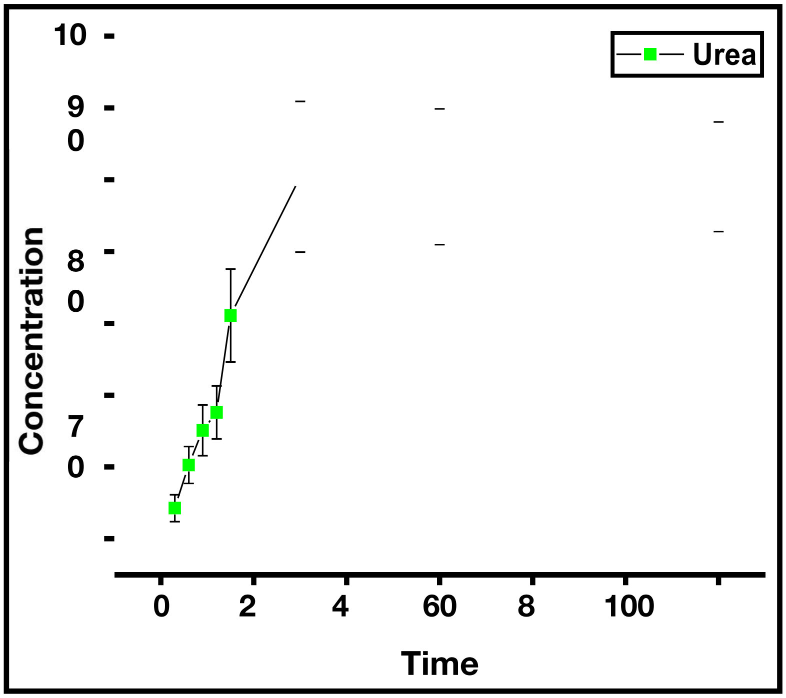


Figure 18 Uncoated Urea Release: Time (min) Vs. Urea Concentration (ppm).

The correlation between untreated urea concentrations (ppm) and time (min) is depicted in **Figure. 19.** 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. 19.**

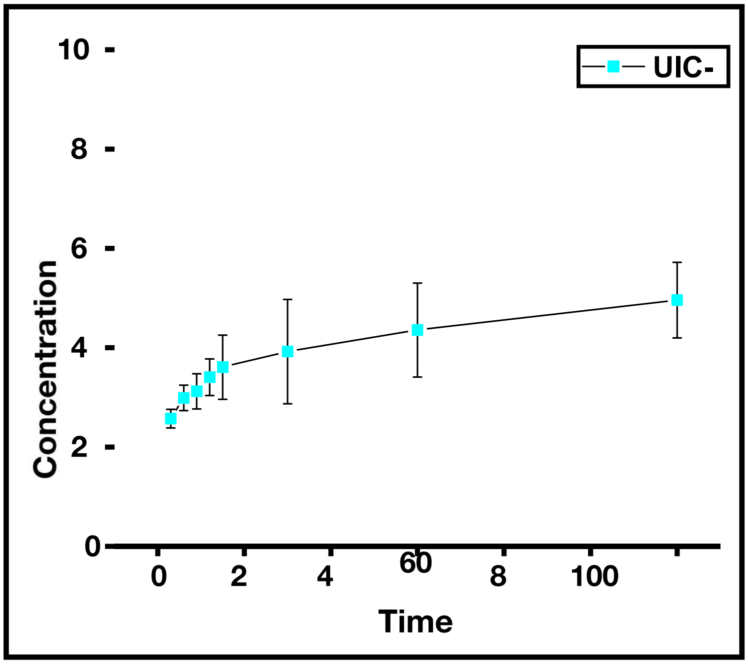


Figure 19 UIC-1 Urea Release: Time (min) Vs. Urea Concentration (ppm).

Figure. 20. 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 slow release and reduce the release rate up to 1.67 times.

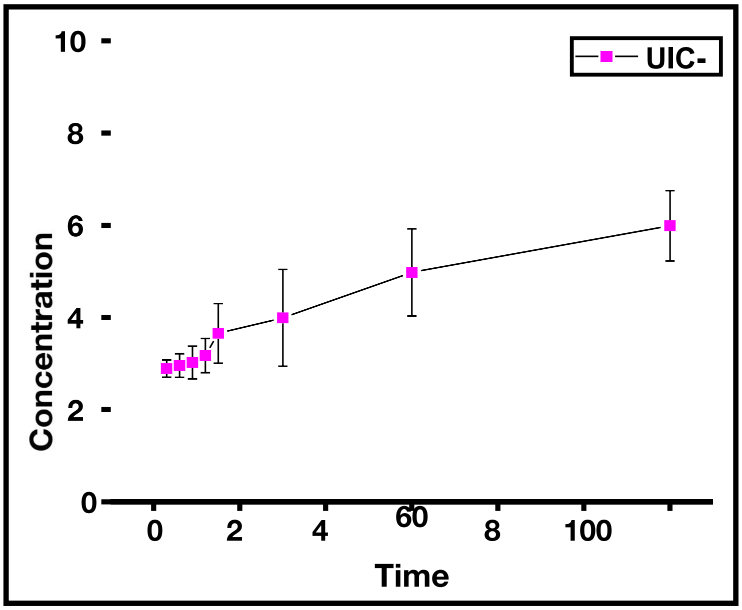


Figure 20 UIC-2 Urea Release: Time (min) Vs. Urea Concentration (ppm)

In contrast, as depicted in Figure. 21. 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.

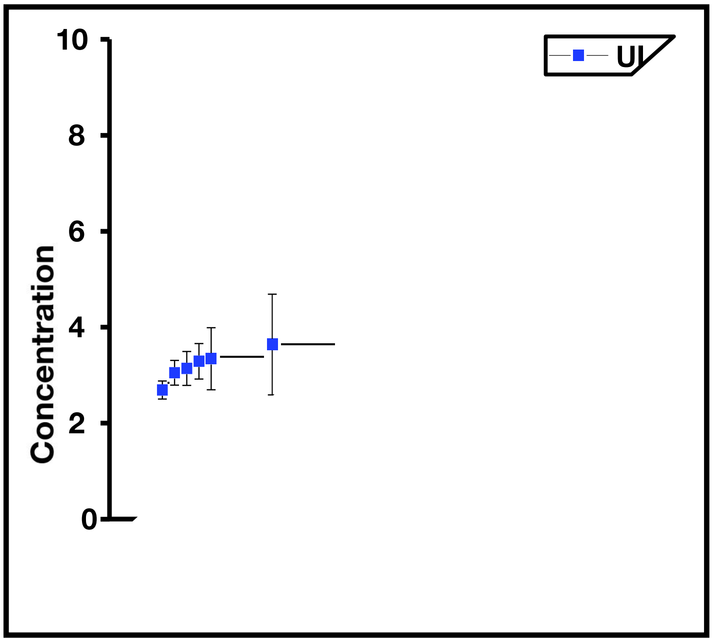


Figure 21 . C-3 Urea Release: Time (min) Vs Urea Concentration (ppm).

Table. 9 and **Figure. 22.** 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 9 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**

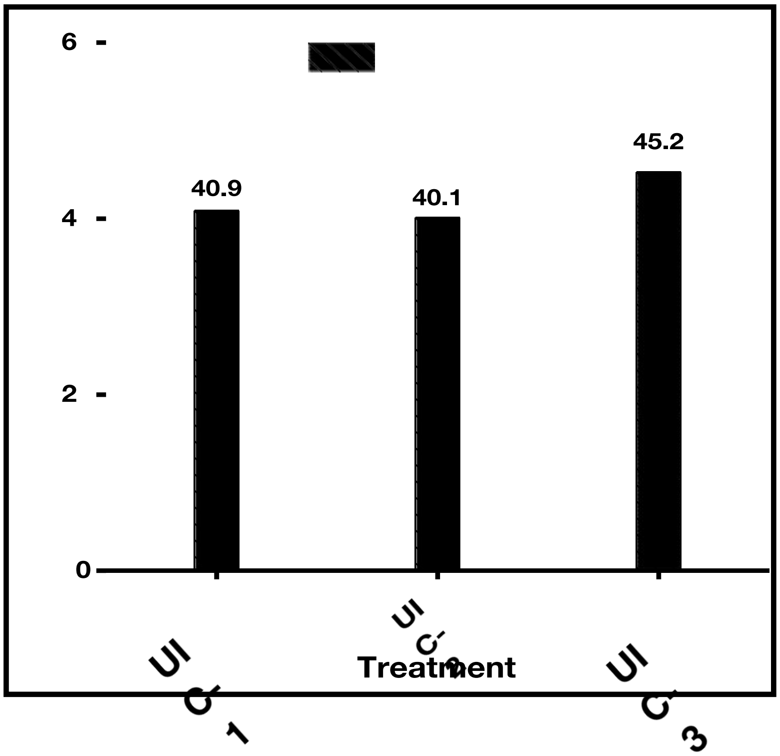


Figure 22 UIC’s Efficiency At 15 Minutes: Samples Vs. Efficiency (%).

4.4 Characterization Of Urea Ionic Co-Crystals

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

4.4.1 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 conficrystal’s EDX analysis.

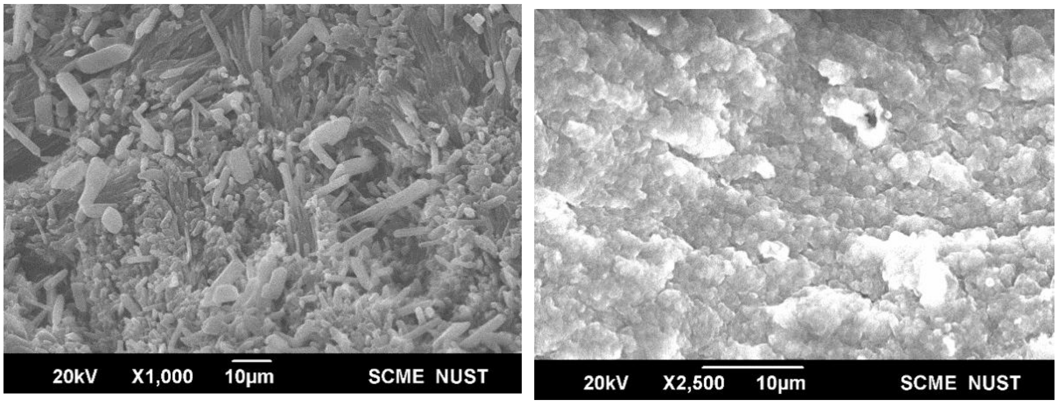


Figure 23 SEM Micrograph of Untreated Urea.

Figure 24. depicts SEM micrograph of UIC-2 treatment having KCl and $ZnCl_2$ 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 of a spongy structure with cluster on someplace because of the union of two film-forming substances.

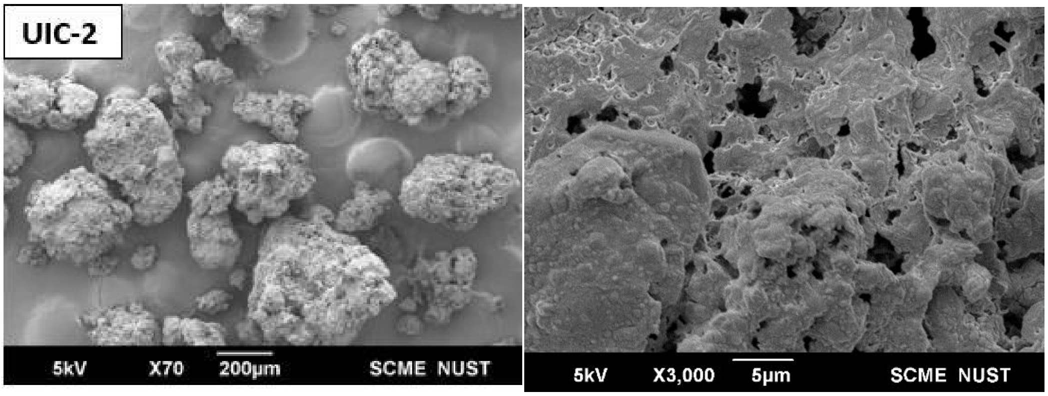


Figure 24 SEM Micrograph of UIC-2 Treatment

4.4.2 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. 25.** At wavelength 3440 and 3344 cm^{-1}, uncoated urea shows asymmetric and symmetric vibrations of NH_2. At wavelength 2925 cm^{-1}, stretching vibrations are exhibited by urea due to the presence of CH and N-H appearances. The peaks in between 2100 cm^{-1} and 2500 cm^{-1} show the stretching vibrations due to C=O. At peak 2011 cm^{-1} bending vibrations are shown by urea which are attributed to the presence of C and H. At peak 1625 cm^{-1} is a carbonyl (CO) and at the peak of 1455 cm^{-1} is a bending vibration NH and CH stretching vibration of $O = C\text{-}NH_2$. Also, the band which appeared at 1455 cm^{-1} is attributed to –CN stretching .At 1159 cm^{-1}, a stretching vibration mode resultant from the –C-O-C group can be seen. C- H overtone stretching vibrations are observed at 1159 cm^{-1}. The peak at 586 cm^{-1} representing the strong stretching vibrations in urea is imputed to the presence of C & H.

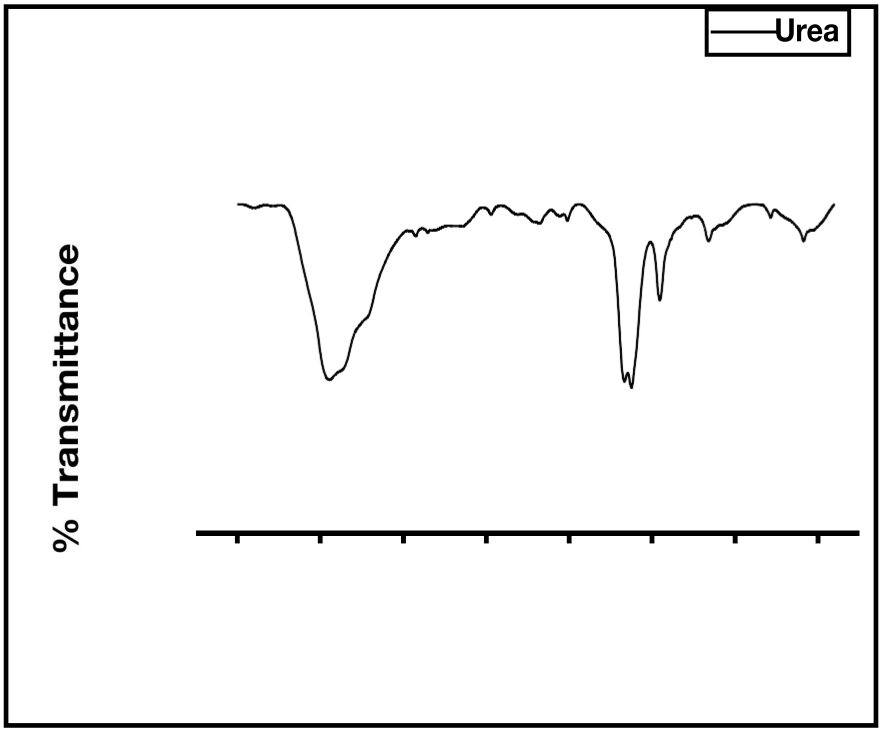


Figure 25 FTIR Spectrum of Untreated Urea

The FTIR spectrum of UIC-1 was given in Figure **26** At wavelength 3458 cm^{-1} and 3348cm^{-1} UIC-1 shows stretching vibration of N-H and O-H like untreated one. At peak 3256 cm^{-1}, the sample shows an OH vibration, which implies water that is absorbed. At peak 2220 cm^{-1} is a Nitrile (C≡N) stretching vibration & peak 2010 cm^{-1} is an Alkyne (C≡C) stretching vibration. At peak 1622 cm^{-1} is a stretching vibration of urea due to carbon atom and keto (C=O) group and at the peak of 1454 cm^{-1} is a bending vibration NH & stretching CH stretching vibration of O = C-NH_2. At peak 1330 cm^{-1} strong vibrations are shown by urea corresponding to the presence of C-N linkage. Also,the band which appeared at 1454 cm^{-1} is attributed to –CN stretching. At 1158 cm^{-1} and 1263 cm^{-1}, a stretching vibration mode resultant from the –C-O-C group can be seen like in untreated urea prill. C-H overtone stretching vibrations are observed at 1158 cm^{-1}. The peaks from 529 cm^{-1} to 780 cm^{-1} shows the C-Cl stretching of halo compounds.

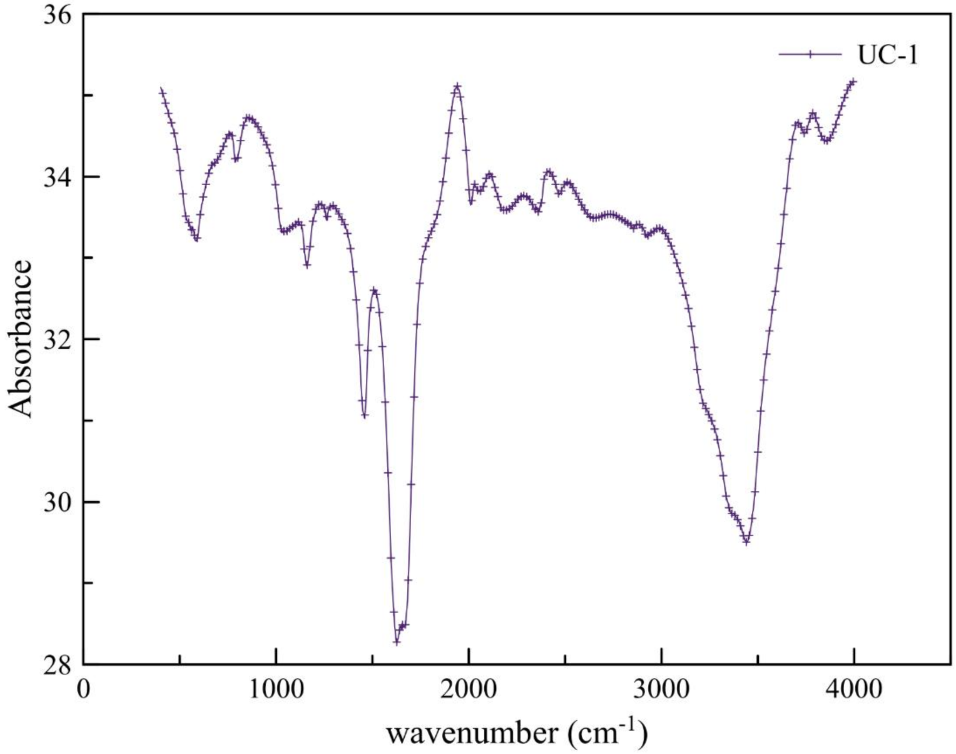


Figure 26 show FTIR Spectrum Of UIC-1.

The FTIR spectrum of UIC-2 was given in **Figure 27.** At wavelength 3450 cm^{-1} and 3357 cm^{-1} UIC-2 shows N-H and O-H stretching vibration like untreated one. At peak 3256 cm^{-1}, the sample shows an O-H vibration, which implied water that is absorbed. At peaks 2422 cm^{-1} and 2216 cm^{-1}, urea shows stretching vibrations due to C-N linkage. The peak at 2009 cm^{-1} is an Alkyne (C≡C) stretching vibration. At peak 1622 cm^{-1} is a Carbonyl (C=O) stretching mode of carbon atom and keto (C=O) group. The peak 1652 cm^{-1}, showing bending vibrations of urea is attributed to the presence of amine (N-H). The peak of 1449 cm^{-1} is a bending vibration NH and CH stretching vibration of O = C-NH_2. Also, the band which appeared at 1449 cm^{-1} is attributed to –CN stretching. At 1156 cm^{-1}, a stretching vibration mode resultant from the –C-O-C group can be seen like in untreated urea prill. C-H overtone stretching vibrations are observed at 1156 cm^{-1}. The peaks from 531 cm^{-1} to 783 cm^{-1} shows the C-Cl stretching of halo compounds. The -ONO2 stretching vibrations appeared between 700 cm^{-1} to 900 cm^{-1} at low-intensity absorption.

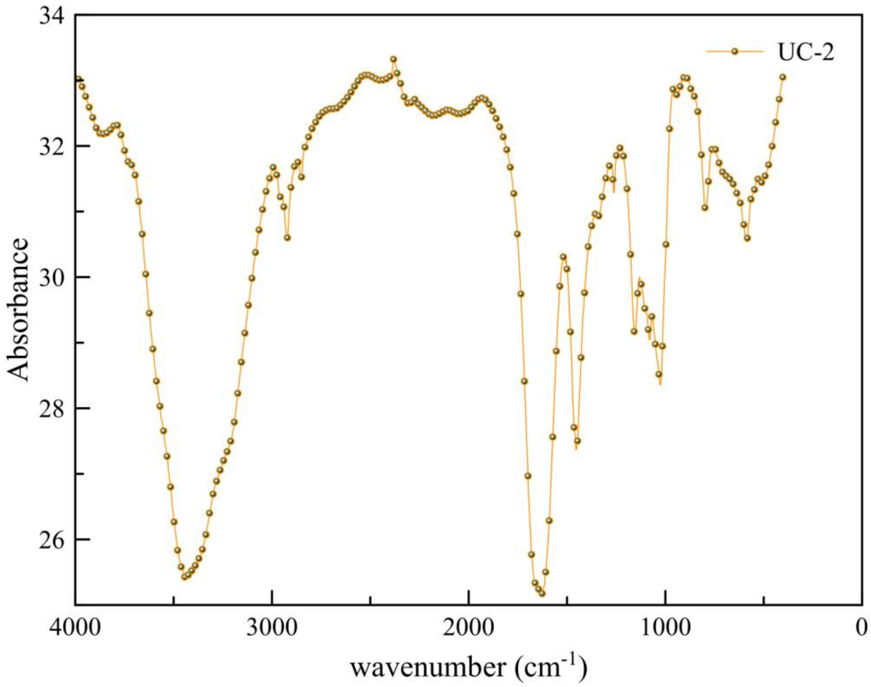


Figure 27 FTIR Spectrum Of UIC-2.

The FTIR spectrum of UIC-3 was given in **Figure 28.** At peak 3936 cm^{-1}, urea shows O-H stretching vibrations. At wavelength 3460 cm^{-1} and 3363 cm^{-1} UIC-3 shows N-H and O-H stretching vibration like untreated one. At peak 3256 cm^{-1}, the sample shows an O-H vibration, which implied water that is absorbed. The peak at 2009 cm^{-1} is an Alkyne (C≡C) stretching vibration. At peak 1623 cm^{-1} is a Carbonyl (C=O) stretching mode of carbon atom and keto (C=O) group. The peak of 1453 cm^{-1} is a bending vibration NH and CH stretching vibration of O = C-NH$_2$. Also, the band which appeared at 1453 cm^{-1} is attributed to with P=O and –CN stretching. The band which appeared at 1158 cm^{-1} is associated with P-OH stretching vibration. At 1158 cm^{-1}, a stretching vibration mode resultant from the –C-O-C group can be seen like in untreated urea prill. C-H overtone stretching vibrations are observed at 1158 cm^{-1}. The peaks from 532 cm^{-1} to 781 cm^{-1} shows the C-Cl stretching of halo compounds. At wavelength 560 cm^{-1} shows PO4 vibration. The O-N=P and -ONO_2 stretching vibrations appeared between 700 cm^{-1} to 900 cm^{-1} at low-intensity absorption bands.

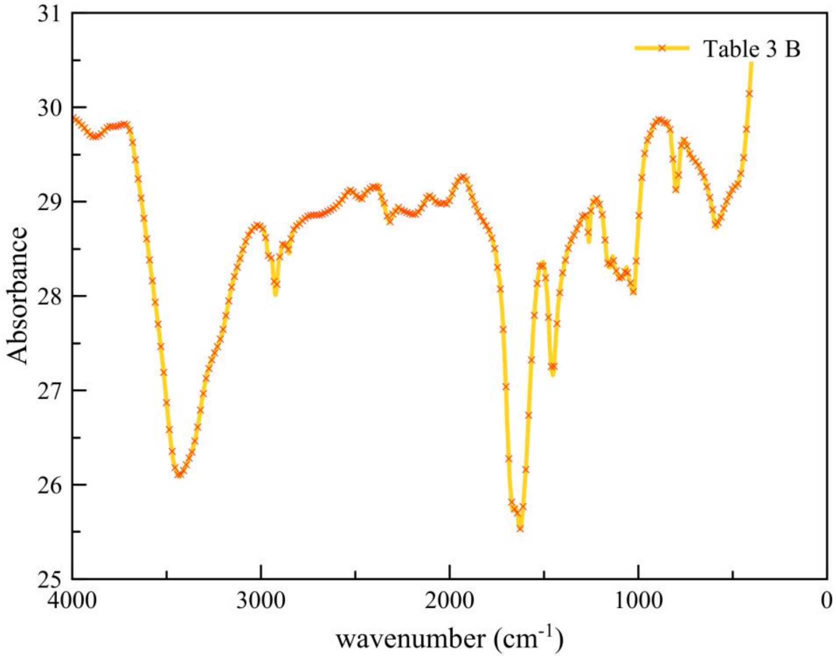


Figure 28 FTIR Spectrum Of UIC-3

4.4.4 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 10 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**

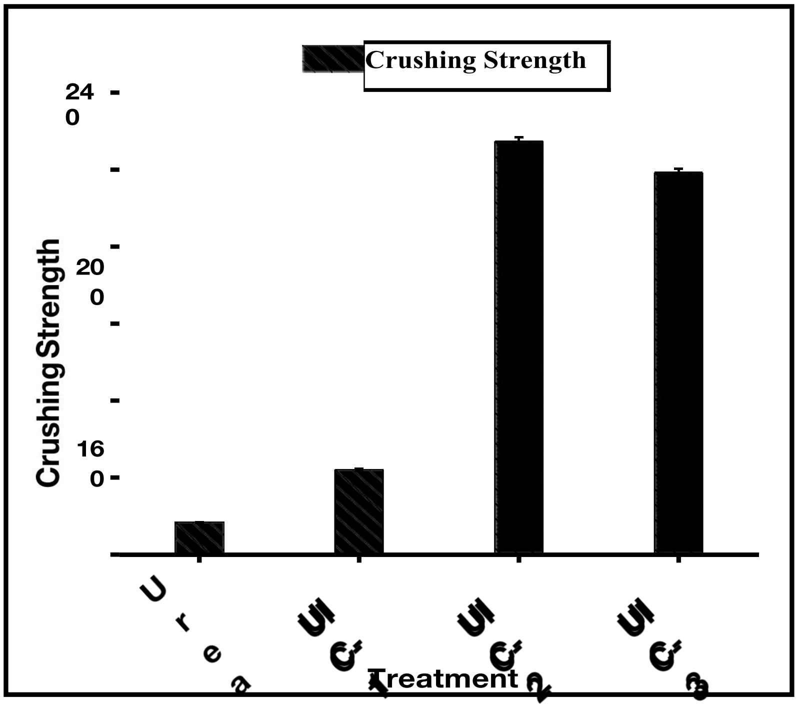


Figure 29 Crushing Strength of Untreated Urea And Urea Ionic Co-Crystals

Figure 30 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.

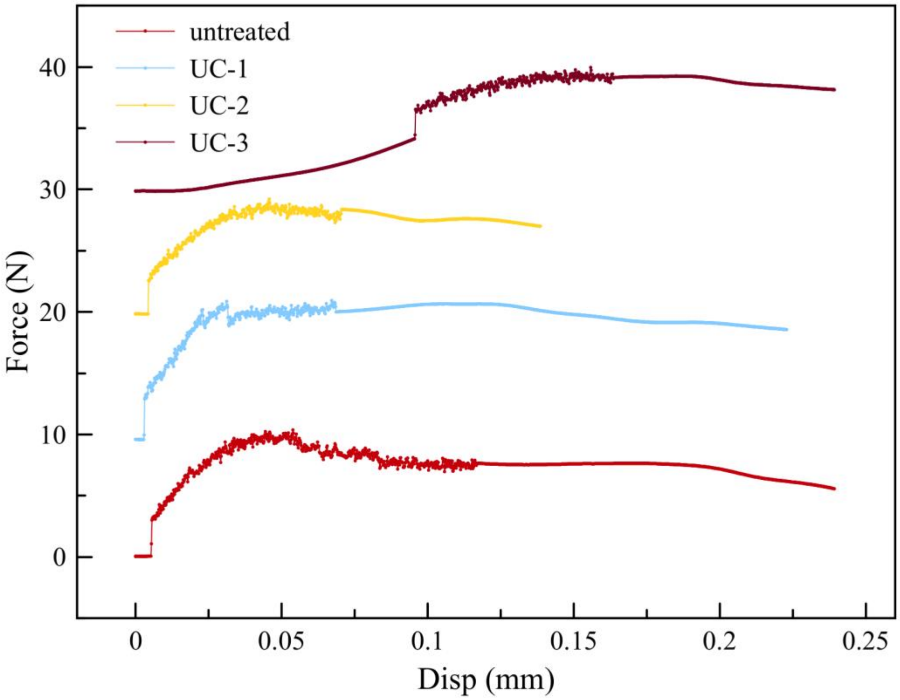


Figure 30 Crushing Strength of Untreated Urea And Urea Ionic Co-Crystals.

4.4.5 X-Ray Diffraction (XRD)

For the examination of crystalline characteristics of laboratory manufactured control release urea fertilizer, 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.

XRD pattern shown in **Figure 31** 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 $CO(NH_2).2HNO_3$ formed .Solid H_2SO_4 $CO(NH_2)_2$ and $H_2SO_4.2CO(NH_2)_2$ accumulating from the leash urea $H_2SO_4.H_2O$ mixture were seen by Dalman at 10 and 25 °C. The crystal structure of

$H_2SO_4.2CO(NH_2)_2$ was not discovered prior to 1999, when Chen et al. discovered that the crystal form is made up of two uranium ions, $CO(NH_2)2H^+$ coupled to nearby 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.

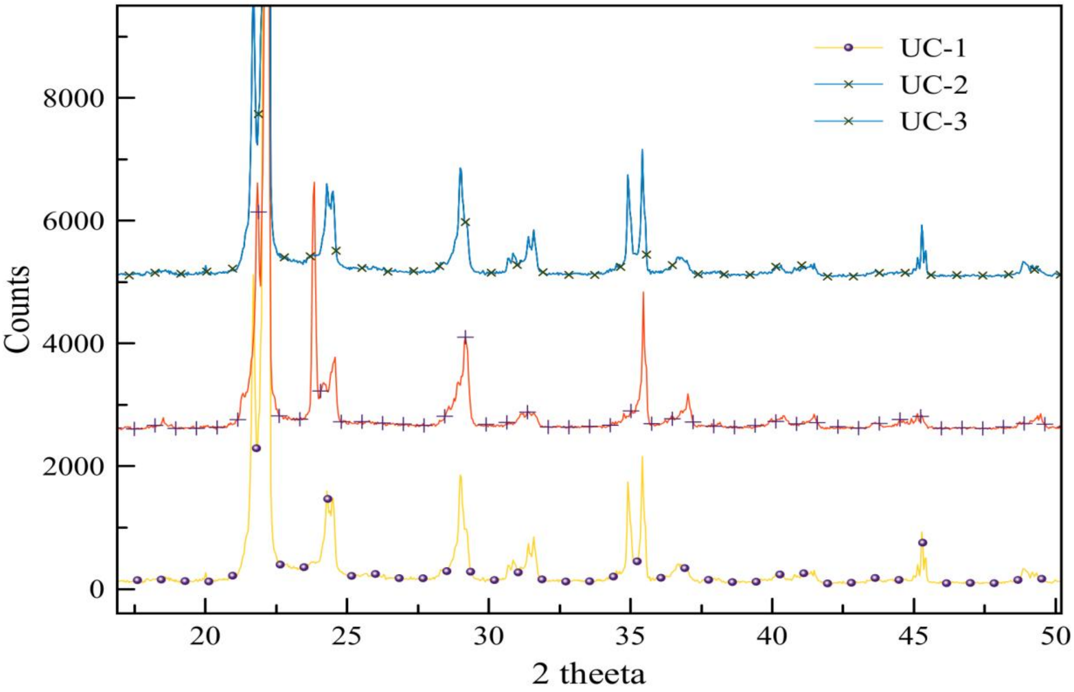


Figure 31 XRD Pattern of Coated Urea

4.5 Soil Analysis

4.5.1 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:

Soil Moisture= $\frac{\boldsymbol{Wet-Dry}}{\boldsymbol{Wet}}\ \boldsymbol{X\ 100}$ **(19)**

Moisture Factor = $\frac{\boldsymbol{Wet\ Soil\ (g)Or\ 100+\%soil\ moisture}}{\boldsymbol{Dry\ Soil\ (g)100}}$ ………………………… **(20)**

The results are presented below in **Table 11.**

Table 11 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**

4.5.2 Water Holding Capacity

Following equation gave the Water holding capacity (WHC)

$$\textbf{100\% Water Holding Capacity} = \frac{W1-W2}{W1} \ \mathbf{x100} \qquad \textbf{(21)}$$

The results are presented as follows:

Table 12 Water Holding Capacity

S. No.	**Weight Of Wet Soil After Drainage (W_1)**	**Weight Of Oven Dry Soil W_a) + Weight Of Pot W_b) = (W_2)**	**100% WHC =** $\frac{\overline{W_1 - W_2}}{W_2} \times 100$
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 × 0.2577 =
515.4 ml For, 65% WHC:

515.4× 0.65 = 335 ml

PH of Soil:

Upon 65 days of planting spinach, a minor reduction in soil pH was observed, as indicated in **Figure 32** 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 fertilizer 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 fertilizers. 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:

4.5.3 Electrical Conductivity (EC) Of Soil

The findings for soil EC is depicted in **Figure 33** 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:

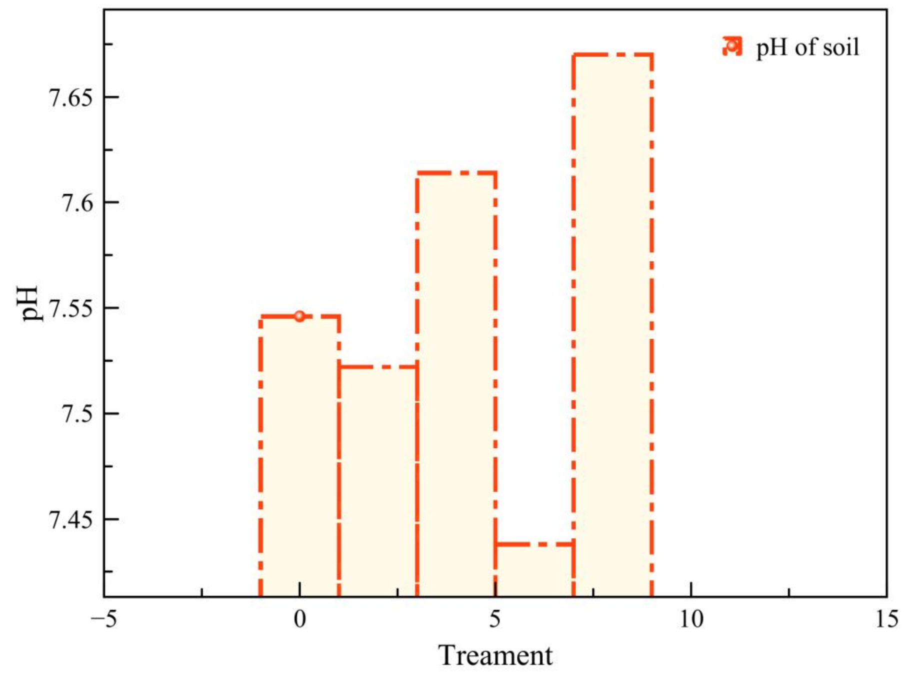


Figure 32 pH Of Soil After the Application Of Urea & Urea Ionic Co-Crystals After 65 Days Of Planting Spinach.

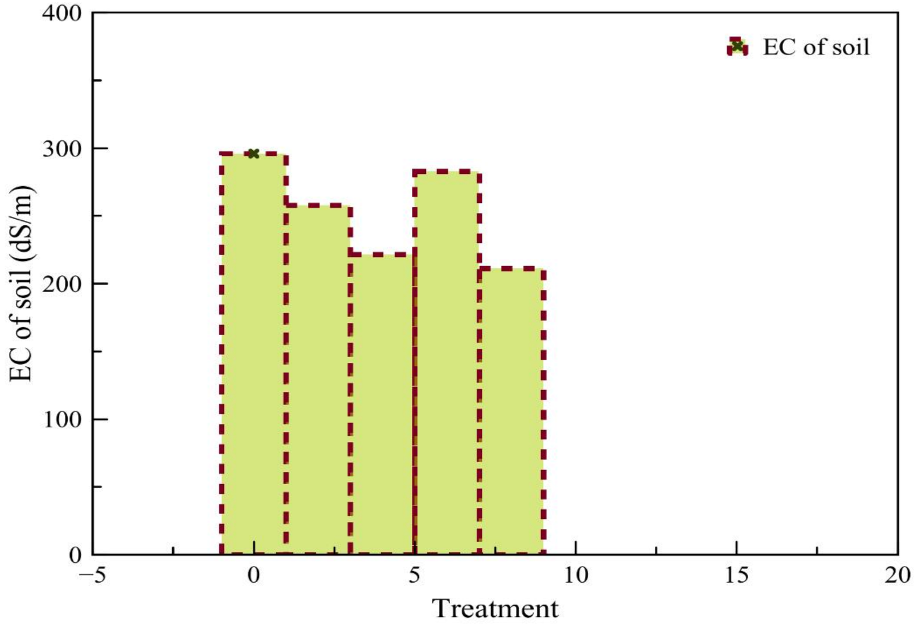


Figure 33 Electrical Conductivity (EC) Of Soil After the Application Of Urea & Urea Ionic Co-Crystals.

4.5.4 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 34** depicts the effect of urea fertilizer and various types of ionic co- crystals urea fertilizer on total organic carbon in soil. The application of fertilizer 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 fertilizer 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:

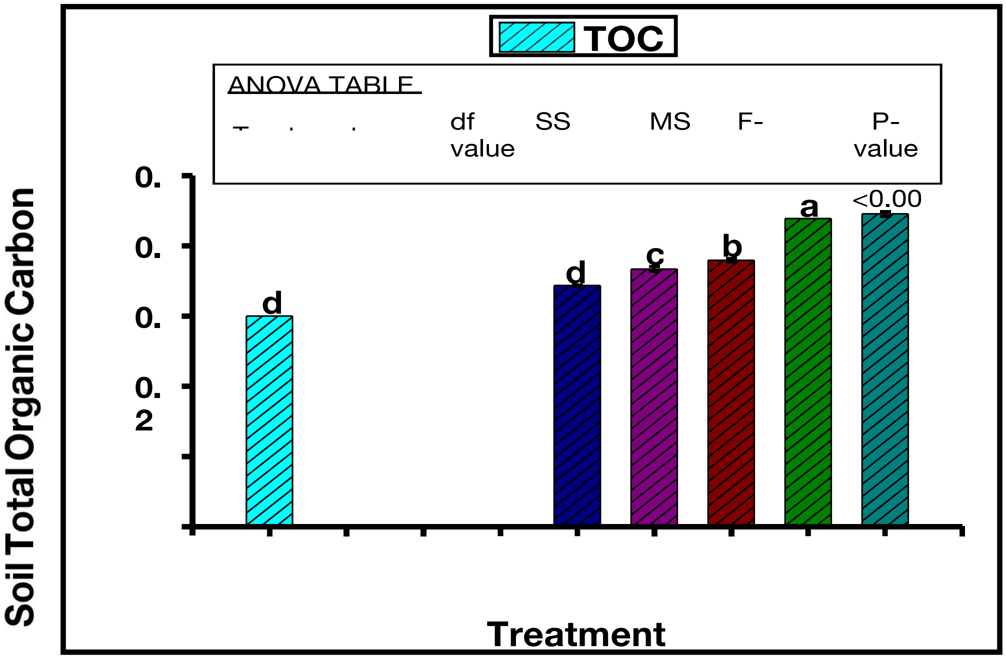


Figure 34 Total Organic Carbon (TOC) Of Soil After The Application Of Urea & Urea Ionic Co-Crystals.

4.5.5 Organic Matter (OM) Of Soil

Figure 35 indicated the Organic Matter of soil that was computed from the total organic carbon of soil with the help of formula given below:

% Organic Matter = 1.724 × (% Total Organic Carbon) ….. (22)

The application of fertilizer 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 fertilizer 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.

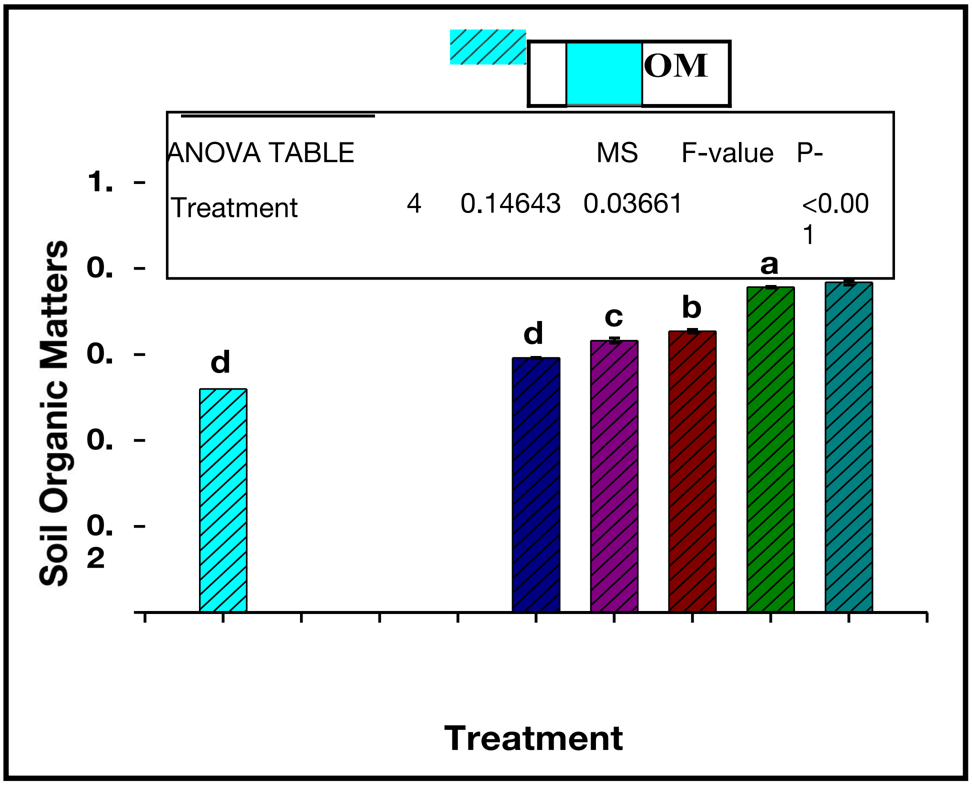


Figure 35 Organic Matter (OM) Of Soil after the Application Of Urea & Urea Ionic Co-Crystals.

4.5.6 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 36** 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 fertilizer 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].

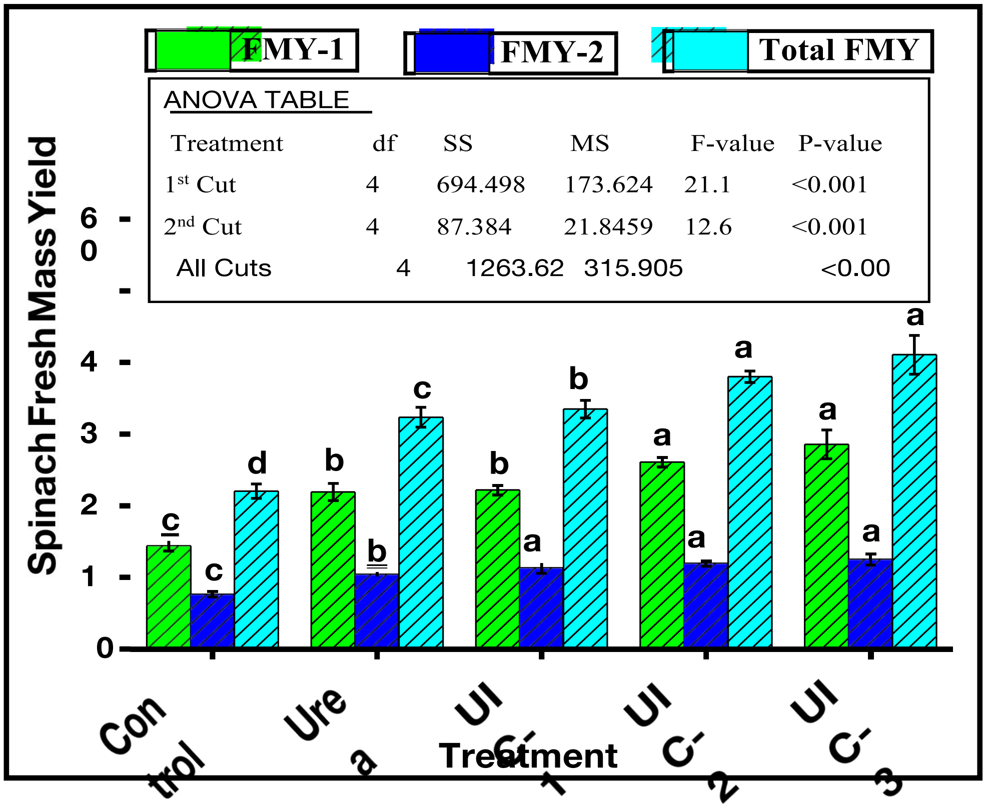
4.5.7 Fresh Matter Yield of Plant

4.5.7.1 Spinach Fresh Mass Yield

Table 13 and **Figure 36** illustrate the response of urea and various types of urea ionic co-crystals fertilizer 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 ± 2.01) and (12.52 ± 0.78) respectively yields the highest spinach fresh matter yield, followed by UIC-2 treatment (26.09 ± 0.67) and (11.93± 0.35) respectively for both harvestings. The control treatment has the lowest spinach fresh matter yield (14.40 ± 0.72) and (7.64 ± 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 13 Effect Of Urea & Urea Ionic Co-Crystals Fertilizer On Spinach Fresh Mass Yield.

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



ANOVA TABLE

Treatment	df	SS	MS	F-value	P-value
1st Cut	4	694.498	173.624	21.1	<0.001
2nd Cut	4	87.384	21.8459	12.6	<0.001
All Cuts	4	1263.62	315.905		<0.00

Figure 36 Fresh Mass Yield Of Spinach After The Application Of Urea & Urea Ionic Co-Crystals.

4.5.7.1 Roots Fresh Mass Yield

Table 14 and **Figure 37** illustrate the response of urea and various types of urea ionic co-crystals fertilizer 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 ± 0.33) yields the highest roots fresh matter yield, followed by UIC-2 treatment (21.29 ± 1.25). The control treatment has the lowest roots fresh matter yield (15.24 ± 0.33). This is due to the absence of compacting materials with urea, that's result in rapid urea release.

Table 14 Effect of Urea & UIC's Fertilizer on Roots Fresh Mass Yield

Treatments	**Roots Fresh Mass Yield (g/pot)**
Control	**15.24 ± 0.33**
Urea	**20.26 ± 0.57**
UIC-1	**20.87 ± 0.22**
UIC-2	**21.29 ± 0.33**
UIC-3	**21.81 ± 1.25**

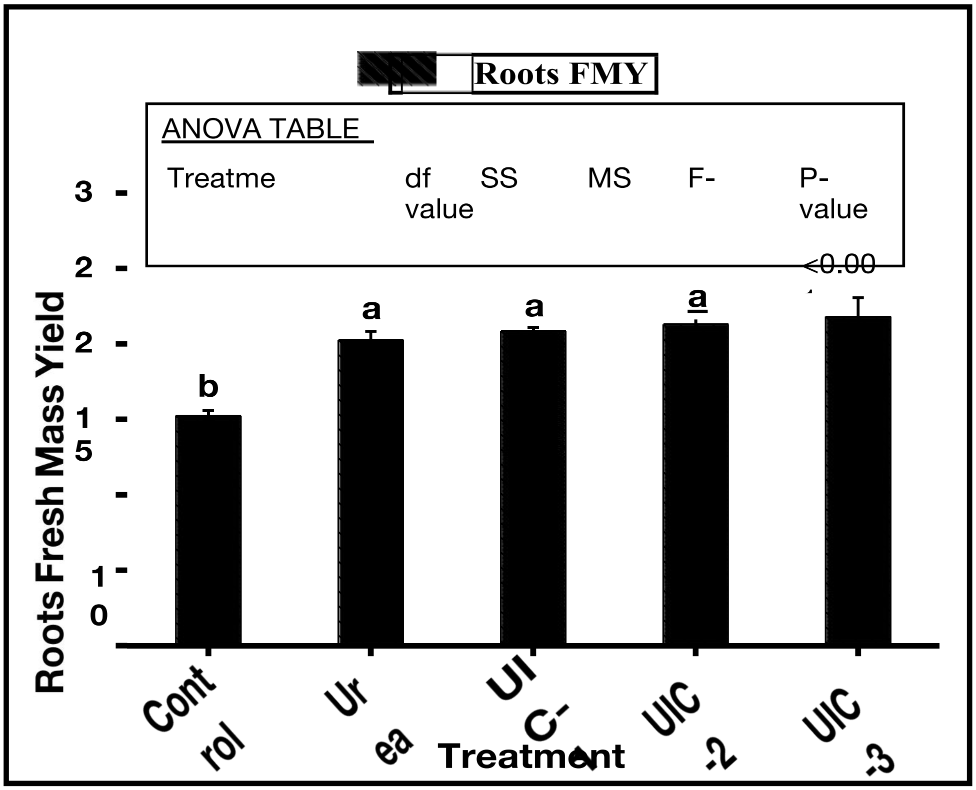


Figure 37 Roots Fresh Mass Yield After the Application of Urea & Urea Ionic Co-Crystals.

4.5.8 Dry Matter Yield of Plant

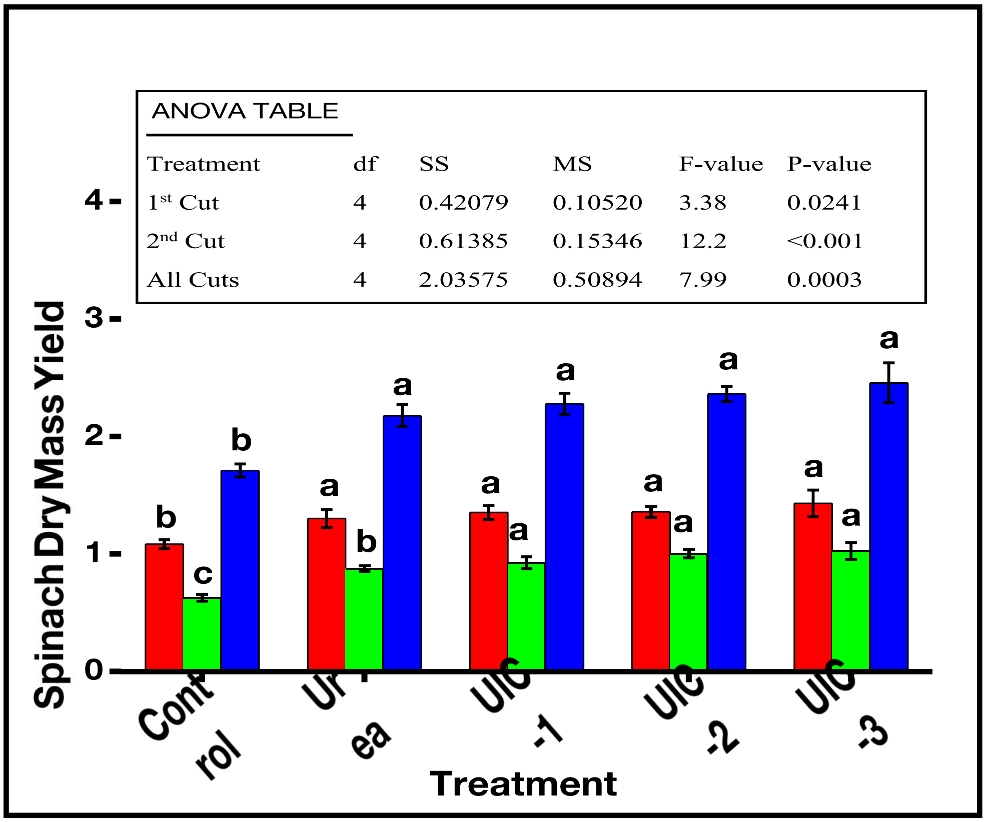
4.5.8.1 Spinach Dry Mass Yield

Table 15 and **Figure 38** 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 ± 0.11) and (1.03 ± 0.07) respectively yields the highest spinach dry matter yield, followed by UIC-2 treatment (1.36 ± 0.05) and (1.00).

± 0.04) respectively for both harvestings. The control treatment has the lowest spinach dry matter yield (1.08 ± 0.04) and (0.63 ± 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 15 Effect of Urea & UIC's Fertilizer on Spinach Dry Mass Yield.

Treatments	**Spinach Dry Mass Yield g/pot)** **(1st Harvest)**	**Spinach Dry Mass Yield g/pot)** **(2nd 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**



ANOVA TABLE

Treatment	df	SS	MS	F-value	P-value
1st Cut	4	0.42079	0.10520	3.38	0.0241
2nd Cut	4	0.61385	0.15346	12.2	<0.001
All Cuts	4	2.03575	0.50894	7.99	0.0003

Figure 38 Dry Mass Yield Of Spinach After The Application Of Urea & Urea Ionic Co-Crystals.

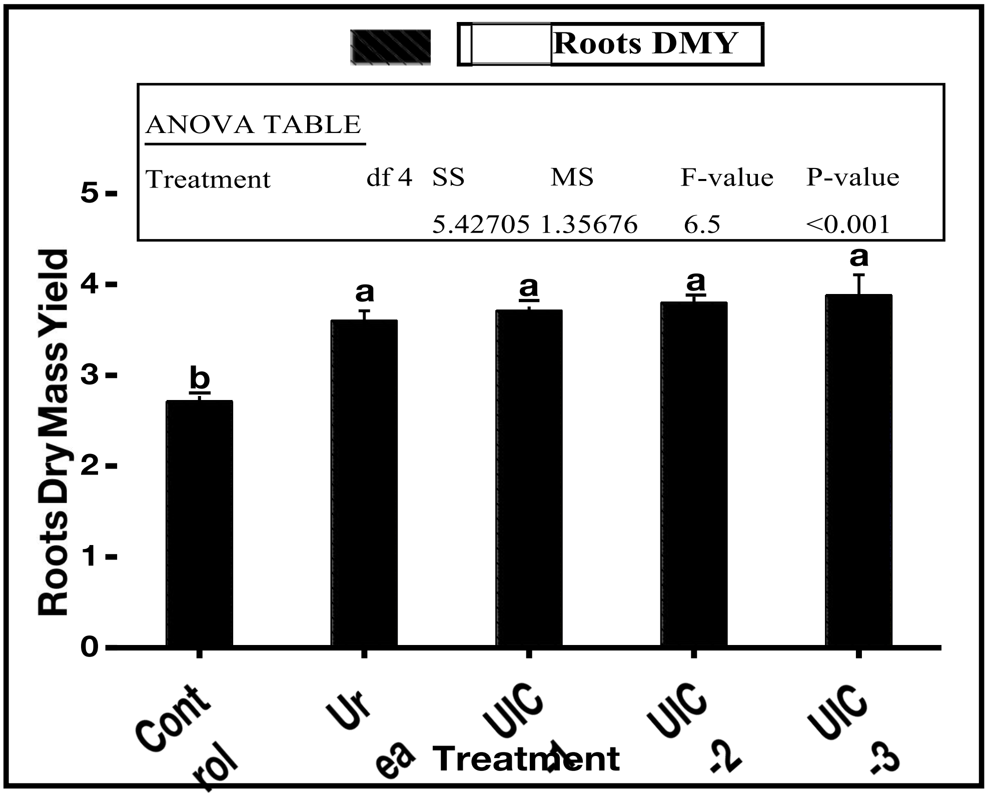
4.5.8.2 Roots Dry Mass Yield

Table 16 and **Figure 39** illustrate the response of urea and various types of urea ionic co-crystals fertilizer 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 ± 0.22) yields the highest roots dry matter yield, followed by UIC-2 (3.80 ± 0.06). The control treatment has the lowest roots dry matter yield (2.72 ± 0.06).

This is due to the absence of compacting materials with urea, that's result in rapid urea release.

Table 16 Effect of Urea & UIC's Fertilizer on Roots Dry Mass Yield.

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



ANOVA TABLE

Treatment	df 4	SS	MS	F-value	P-value
		5.42705	1.35676	6.5	<0.001

Figure 39 Roots Dry Mass Yield After the Application Of Urea & Urea Ionic Co-Crystals.

4.5.9 Chlorophyll Contents

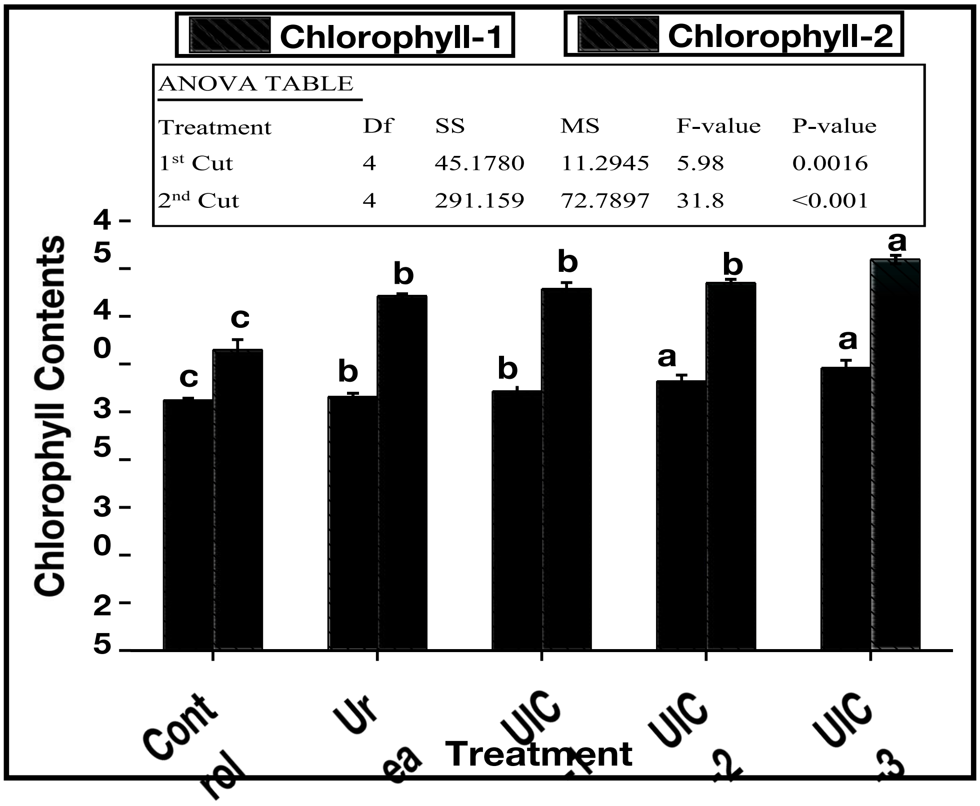
The bulk of chlorophyll per unit area computes the photosynthetic potential of a plant. There is a straight relation between the soil's nitrogen availability and chlorophyll in plants. In fertilizer management, chlorophyll can be utilized as a secondary standard of levels of nitrogen.

4.5.1.1 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 ± 0.80) and (40.95 ± 0.43) respectively for both harvestings and is followed by UIC-2 (28.2 ± 0.65) and (38.5 ± 0.39) respectively for both harvestings. Control treatment gives a figure of (26.22 ± 0.21) and (31.52 ± 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 17** and **Figure 40** depicts the chlorophyll content of all samples, during both harvestings.

Table 17 Effect of Urea & Urea Ionic Co-Crystals Fertilizer on Plant Chlorophyll Content.

Treatments	**Plant Chlorophyll Content µg/g) (1st Harvest)**	**Plant Chlorophyll Content µg/g) (2nd Harvest)**
Control	**26.22 ± 0.21**	**31.52 ± 1.04**
Urea	**26.57 ± 0.40**	**37.12 ± 0.27**
UIC-1	**27.15 ± 0.56**	**37.88 ± 0.64**
UIC-2	**28.20 ± 0.65**	**38.50 ± 0.39**
UIC-3	**29.60 ± 0.80**	**40.95 ± 0.43**



ANOVA TABLE

Treatment	Df	SS	MS	F-value	P-value
1st Cut	4	45.1780	11.2945	5.98	0.0016
2nd Cut	4	291.159	72.7897	31.8	<0.001

Figure 40 Chlorophyll Contents After The Application Of Urea & Urea Ionic Co-Crystals.

4.5.9.2 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 µg/g), and is followed by UIC-2 (27.08 µg/g). Control treatment gives a figure of (19.33 µg/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 fertilizers in this experiment. **Table 18** and **Figure 41** depicts the chlorophyll values a, b, and total chlorophyll of all samples, during both harvestings.

Table 18 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**

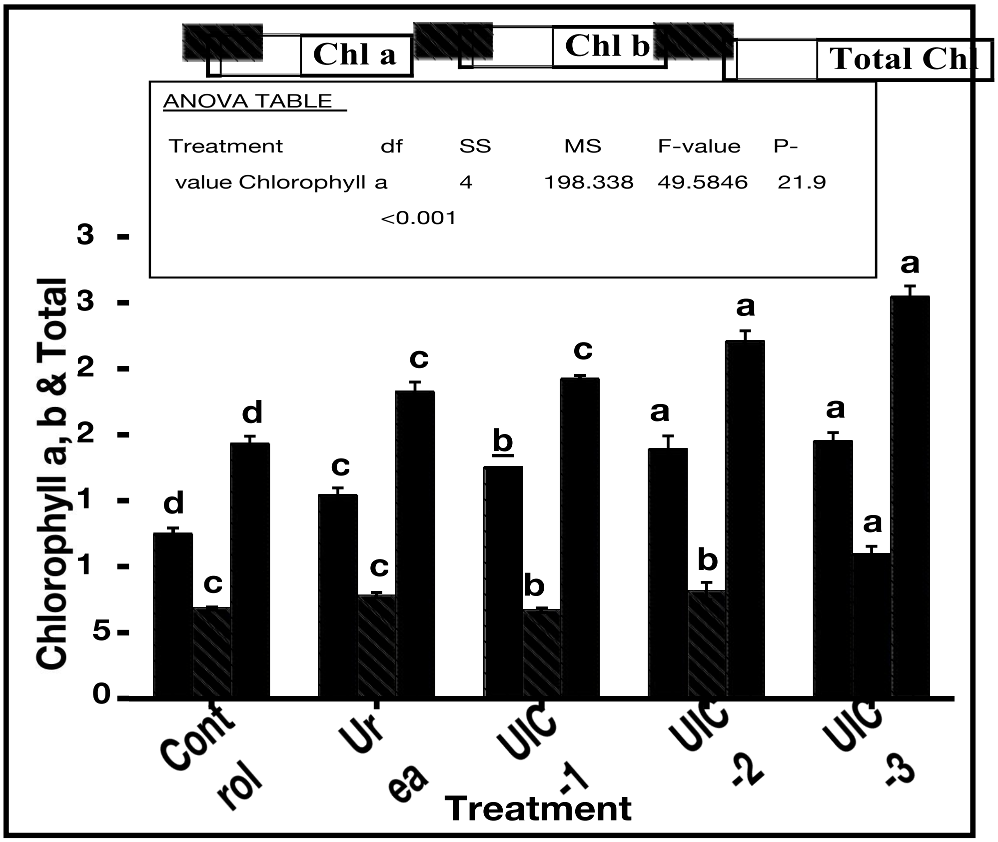


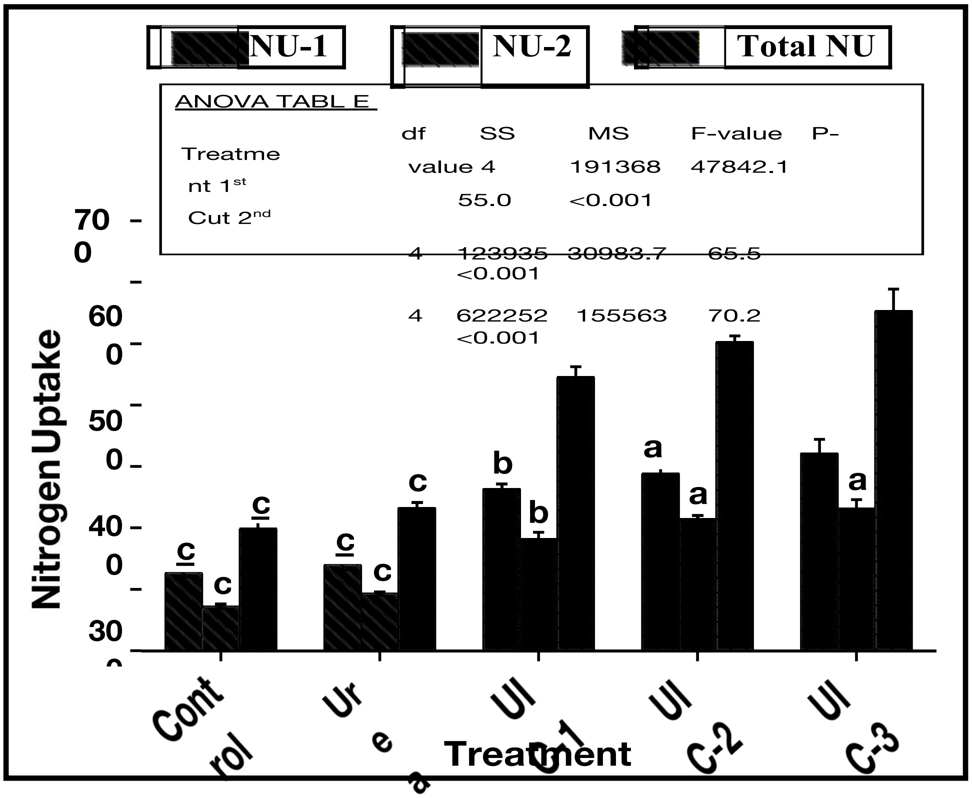
Figure 41 Chlorophyll a, b & Total After The Application Of Urea & Urea Ionic Co-Crystals

4.5.10 Nitrogen Uptake

The nitrogen content of the crops is represented via nitrogen uptake. **Table 19** and **Figure 42** provides data on plant uptake of nitrogen. In comparison to the control, urea fertilizer treatments showed a considerable increase in N uptake. In comparison to various urea ionic co-crystal fertilizer 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 urea ionic co-crystals fertilizer to untreated urea value, there is a 109.02 % and 124.37 % rise respectively after both harvestings.

Table 19 Effect of Urea & Urea Ionic Co-Crystals Fertilizer on Plant Nitrogen Uptake.

Treatments	**Plant Nitrogen Uptake (mg/kg) (1st Harvest)**	**Plant Nitrogen Uptake (mg/kg) (2nd 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**



ANOVA TABL E
df SS MS F-value P-
Treatme value 4 191368 47842.1
nt 1st 55.0 <0.001
Cut 2nd
4 123935 30983.7 65.5
<0.001
4 622252 155563 70.2
<0.001

Figure 42 Plant Nitrogen Uptake After The Application Of Urea & Urea Ionic Co-Crystals.

4.5.11 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 43** depicts all of the ANR findings.

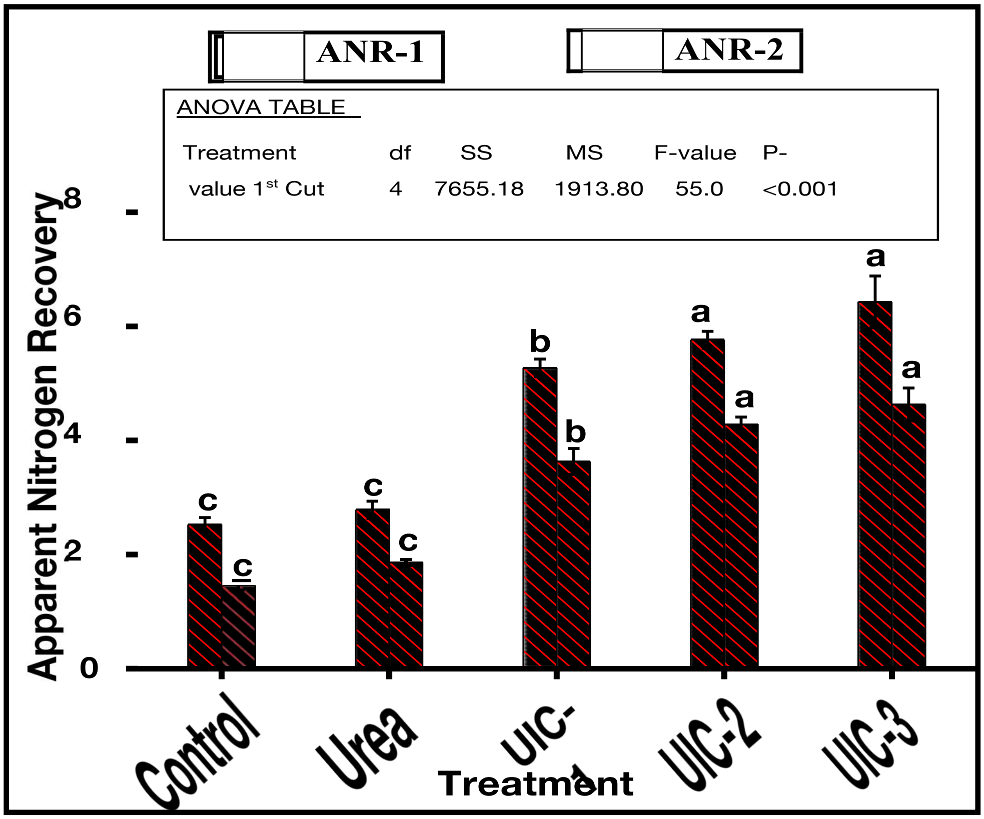


Figure 43 Apparent Nitrogen Recovery After The Application Of Urea & Urea Ionic Co-Crystals.

4.6 Plants Growth

The growth of spinach plants during the whole period (0 to 65 days) during both the harvestings are shown as following in **Figure 44.**

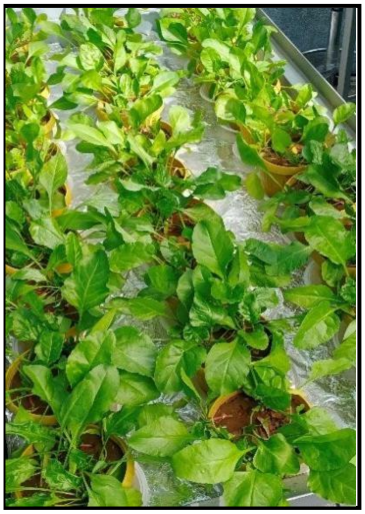
Day-1 (Sowing)

Day-7 Of Sowing

Day-15 Of Sowing

Day-22 Of Sowing

Day-29 Of Sowing



Day-35 Of Sowing

Day-35 (1st Harvesting) Day-7 Of 1st Harvest Day-15 Of 1st Harvest

Day-22 Of 1st Harves **Day-29 Of 1st Harvest** **Day-65 (2nd Harvesting)**

Figure 44 Experimental view of different treatment section of plant

4.6.1 Nitrogen analysis in Plant and Soil:

To analyze the estimated by micro–Kjeldahls method. The **Table 20** illustrates the percentage of nitrogen in the soil as well as in plants. The result elaborates that nitrogen content was high (0.054) in T4R4 and in Plants, higher concentration of nitrogen presents in T2R2.

Table 20 Analysis of nitrogen with different treatment of plant and soil

Sr No	**Sample code**	**Total Nitrogen(%)**	
		Soil	**Plant**
1	TOR1	0.025	2.47
2	TOR2	0.038	2.36
3	TOR3	0.032	2.39
4	TOR4	0.039	2.56
5	TOR5	0.039	2.75
6	T1R1	0.044	2.57
7	T1R2	0.050	2.84
8	T1R3	0.042	2.29
9	T1R4	0.041	2.19
10	T1R5	0.044	2.48
11	T2R1	0.053	2.33
12	T2R2	0.047	2.22
13	T2R3	0.045	2.33
14	T2R4	0.052	2.18
15	T2R5	0.028	2.30
16	T3R1	0.050	2.61
17	T3R2	0.049	2.51
18	T3R3	0.047	2.28
19	T4R4	0.054	2.48
20	T4R5	0.053	2.42
21	T4R1	0.046	2.22
22	T4R2	0.047	2.30
23	T4R3	0.046	2.21
24	T4R4	0.047	2.37
25	T4R5	0.048	2.18

4.7 Heavy Metal Analysis:

The iron detection in various samples of the plant is analyzed through Atomic Adsorption spectroscopy shown in **Table 21**. The result shows that the percentage of iron (7.295 mg/L) in T_2R is as compared to other treatments.

Table 21 Analysis of iron in different treatment section

Sr.	**Metal(s)**	**Iron (Fe)**
	Module	**Flame**
	Detection limit	**0.004**
	Unit	mg/L
1	T_0R	4.497
2	T_0R	4.495
3	T_0R	4.498
4	T_0R	4.496
5	T_0R	4.493
6	T_1R	4.539
7	T_1R	4.536
8	T_1R	4.537
9	T_1R	4.538
10	T_2R	7.297
11	T_2R	7.295
12	T_2R	7.296
13	T_2R	7.298
14	T_3R	4.842
15	T_3R	4.843
16	T_3R	4.844
17	T_3R	4.845
18	T_4R	4.801
19	T_4R	4.802
20	T_4R	4.803
21	T_4R	4.808

4.8 Release Kinetics

4.8.1 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 were 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 22** and after that put on to the Sinclair and Peppa's formula, modified hyperbola formula, modified Schwartz formula, and Schwartz and Sinclair formula.

Table 22 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**

4.8.2 Sinclair and Peppa's Model

To estimate the release rate from spherical dimensions, Sinclair and Peppa's Model is usually applied as shown in **Table. 23.** 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:

$Q_t = Kt^n$ …….. (23).

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

Table 23 Release Kinetics Data At 25 °C: Sinclair And Peppa’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**

4.8.3 Modified Hyperbola Formula

Modified hyperbola formula, described by the following kind, and results are shown in Table. 24 at

$Q_t = \frac{}{1+bt}$ …….. (24)

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

Table 24 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**

4.9 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. 25.**

$Q = (1 - e^{-bt})$ **…….. (25)**

Table 25 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**

4.10 Modified Schwartz Formula

Illustrated as under is the Modified Schwartz formula with the following form and results are shown in **Table. 26.**

$$Q = a\,(1 - e^{-bt}) \qquad (26)$$

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 26 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. respectively. It is depicted in Table. 26, 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 Peppa'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.

Conclusion

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 uncompacted 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 totally haphazard block motif with six copies. 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 show 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^2 and 20623 cm/m^2), and leaf area index (3.46 m/m^2 and 2.06 m/m^2) 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.

Future 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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