SUSTAINABLE NUTRIENT DELIVERY SYSTEM: INTEGRATING ZINC DOPED CARBON QUANTUM DOTS AND BIOBASED POLYMER FOR ENHANCED UREA FERTILIZER EFFICIENCY

By

Zainab Rahim

(Registration No: 00000402518)

Institute of Environmental Sciences & Engineering

School of Civil & Environmental Engineering

National University of Sciences & Technology (NUST)

Islamabad, Pakistan

(2024)

SUSTAINABLE NUTRIENT DELIVERY SYSTEM: INTEGRATING ZINC DOPED CARBON QUANTUM DOTS AND BIOBASED POLYMER FOR ENHANCED UREA FERTILIZER EFFICIENCY

By

Zainab Rahim

(Registration No: 00000402518)

A thesis submitted in partial fulfillment of the requirement for the degree of

Master of Science in

Environmental Sciences

Supervisor: Dr. Muhammad Ansar Farooq

Institute of Environmental Sciences & Engineering

School of Civil & Environmental Engineering

National University of Sciences & Technology (NUST)

Islamabad, Pakistan

(2024)

Approval Certificate

It is certified that the contents and form of the thesis entitled

"Sustainable Nutrient Delivery System: Integrating Zinc Doped Carbon Quantum Dots And Biobased Polymer For Enhanced Urea Fertilizer Efficiency"

Submitted by

Ms. Zainab Rahim

Has been found satisfactory for partial fulfilment for the requirements of the degree of Master of Science in Environmental Sciences.

Supervisor: ………………………………

Dr. Muhammad Ansar Farooq

Associate Professor

SCEE (IESE), NUST

Dr. Muhammad Ansar Farooq
Associate Professor
SCEE (IESE) NUST
H-12 Islamabad

Co-Supervisor: ………………………………

Dr. Hassan Anwer

Assistant Professor

SCEE (IESE), NUST

Dr. Hassan Anwer
Assistant Professor
IESE (SCEE) NUST Islamabad

31/12/24

GEC Member: ………………………………

Prof. Dr. Muhammad Arshad

Professor/Associate Dean

SCEE (IESE), NUST

PROF DR MUHAMMAD ARSHAD
Associate Dean SCEE (IESE)
NUST H-12, Islamabad

GEC Member: ………………………………

Dr. Aamir Alaud Din

Assistant Professor

SCEE (IESE), NUST

Dr. Aamir Alaud Din
Assistant Professor
IESE (SCEE) NUST Islamabad

THESIS ACCEPTANCE CERTIFICATE

Certified that final copy of MS Thesis written by Ms Zainab Rahim (Registration No. 00000402518), of (SCEE-IESE) has been vetted by undersigned, found complete in all respects as per NUST Regulations, is free of plagiarism, errors, and mistakes and is accepted as partial fulfilment for award of master's degree. It is further certified that necessary amendments as point out by GEC members and evaluators of the scholar have also been incorporated in the said thesis.

Signature: ______________________

Name of Supervisor: Dr. Muhammad Ansar Farooq

Date: 19/12/2024

Dr. Muhammad Ansar Farooq
Associate Professor
SCEE (IESE) NUST,
H-12 Islamabad

Dr. Zeshan
Tenured Professor
HoD Environmental Sciences
SCEE (IESE) NUST Islamabad

Signature (HOD): ______________________

Date: 30/12/2024

Signature (Associate Dean): ______________________ 31/12/24.

PROF DR MUHAMMAD ARSHAD
Associate Dean SCEE (IESE)
NUST H-12, Islamabad

Date: ______________________

Signature (Principal & Dean SCEE): ______________________

Date: 31 DEC 2024

PROF DR MUHAMMAD IRFAN
Principal & Dean
SCEE, NUST

AUTHOR'S DECLARATION

I hereby state that my MS thesis titled "**Sustainable nutrient delivery system: integrating zinc doped carbon quantum dots and biobased polymer for enhanced urea fertilizer efficiency**" is my own work and has not been submitted previously by me for taking any degree from National University of Sciences and Technology, Islamabad or anywhere else in the country/ world.

At any time if my statement is found to be incorrect even after I graduate, the university has the right to withdraw my MS degree.

Name of Student: Zainab Rahim

Date: 19-12-24

PLAGIARISM UNDERTAKING

I solemnly declare that research work presented in the thesis titled "Sustainable nutrient delivery system; integrating zinc doped carbon quantum dots and biobased polymer for enhanced urea fertilizer efficiency" is solely my research work with no significant contribution from any other person. Small contribution/help wherever taken has been duly acknowledged and that complete thesis has been written by me.

I understand the zero-tolerance policy of the HEC and National University of Sciences and Technology, Islamabad towards plagiarism. Therefore, I as an author of the above titled thesis declare that no portion of my thesis has been plagiarized and any material used as reference is properly referred/cited.

I undertake that if I am found guilty of any formal plagiarism in the above titled thesis even after the award of MS degree, the University reserves the right to revoke/withdraw my MS degree and that HEC and NUST, Islamabad has the right to publish my name on the HEC/University website on which names of students are placed who submitted plagiarized thesis.

Name: Zainab Rahim

Signatures: 19-12-24

ACKNOWLEDGEMENTS

To the highest God be glory great things He has done. I acknowledge Your great provisions, protections, and support throughout this course. I am also thankful to my supervisor Dr. Muhammad Ansar Farooq SCEE (IESE) for his appreciation, constructive suggestions, criticisms, and encouragement. My gratitude goes to my co-supervisor Dr. Hassan Anwer SCEE (IESE) for giving his valuable time in department discussion and suggestions to improve the research work.

I remain indebted to the committee members, Prof. Dr. Muhammad Arshad SCEE (IESE) and Dr. Aamir Alaud Din SCEE (IESE) for providing their beneficial suggestions and comments in the context of research and thesis. My appreciation goes to the entire faculty, the staff of SCEE (IESE), and all my lab mates for the support and guidance they provided me during research. My appreciation also goes to my parents and friends for their efforts, moral support, and suggestions towards my progress in life.

Zainab Rahim

DEDICATION

This dissertation is dedicated to the memory of my grand parents, Haji Fateh Muhammad and Sabra Bibi. Although they were one of my strongest motivations to pursue my education, they were unable to see my graduation. This is for them.

I dedicate this dissertation to my parents and siblings Hashim, Haider and Aqsa who inspired my pursuit of environmental sciences. And helped me in all things great and small and encouraged me to pursue my dreams and finish my dissertation.

Thank you to my academic adviser who guided me in this process and the committee who kept me on track.

Zainab Rahim

Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

IPN	Interpenetrating Polymer Network
CQDs	Carbon Quantum Dots
ZnCQDs	Zinc Doped Carbon Quantum Dots
NUE	Nitrogen Use Efficiency
LCS	Liquified Cotton Straw
BPU	Bio-polyurethane coated urea
DCRF	Dual Coated Control Release Fertilizer
FTIR	Fourier-transform infrared spectroscopy
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
EDX	Energy-dispersive X-ray spectroscopy
TKN	Total Kjeldahl Nitrogen
AAS	Atomic absorption spectroscopy
Zn	Zinc
PAPI	Polymeric 4,4’-Methylenediphenyl Diisocyanate
MDI	Methylene diphenyl diiso

ABSTRACT

The increasing demand for sustainable agricultural practices necessitates the development of advanced fertilizers that can efficiently deliver nutrients while minimizing environmental impact. In this study, a dual-coated fertilizer was developed to enhance the efficiency of urea by coating bio-based polymer derived from cotton stalk and subsequently zinc-doped carbon quantum dot (Zn-CQDs) integrated in a hydrogel. This innovative approach addresses the need for controlled N release and tailored Zn supplementation, essential for optimal plant growth, human health, and environmental sustainability. Characterization of Zn-CQDs confirmed successful Zn doping, with XRD peaks between 30° to 35° indicative of crystalline graphitic layers and ZnO, while FTIR spectra revealed the presence of key functional groups. Furthermore, SEM images displayed well-attached zinc oxide particles on spherical carbon dots, further corroborated by EDX analysis showing the presence of C, N, O, and Zn elements. At the next step, the prepared dual-coated fertilizer was evaluated following ISO-standards for slow N release characteristics over 28 d in both water and sand columns. Aliquots were collected and quantified for N contents using Total Kjeldahl N (TKN) and Zn via Atomic Absorption Spectrophotometer. Cumulative N release was almost 75% in 28 days, while cumulative Zn release was up to 1ppm in both water and sand. They are following the ISO standards and fertilizer Zn demand. Future studies should focus on performing controlled lab tests on selected major crops followed by field experiments aiming to enhance crop yields and meet food security targets.

Keywords: Carbon quantum dots, zinc, controlled release fertilizer, biobased polymer

CHAPTER-I INTRODUCTION

1.1 INTRODUCTION

1.1.1 Background:

The exponentially growing population with advanced standards of living, demands a significant rise in the global food demand which poses greater challenges for agricultural resources and the environment. During the years 1850-2011, the global population rushed by seven times (Gu et al., 2021), with the prediction that Africa will be a major contributor to the world population by 2050 (approximately 1.3 billion) followed by Asia (approximately 0.9 billion) where India (24.3%) and China (16.7%) are the prime contributors to the increasing food demand (Alexandratos & Bruinsma - FAO, 2012). It is predicted that the food demand will increase to 62% in the next three decades and the current potential of agriculture is not enough to meet the future food demand. Hence, 60% rapid and sustainable agricultural development is required (Dubey et al., 2020).

Different types of chemical fertilizers, majorly urea fertilizers, are used to increase crop yields. They are user-friendly and the most significant N-source contributing to fulfilling 73.4% of global N-requirement (Pahalvi et al., 2021). The major problem related to urea application is huge N-loss (20-60%) and reduces Nitrogen use efficiency- NUE (30-40%) (Klimczyk et al., 2021).

When urea is applied to soil, the urease enzyme present in the organic matter and microbes hydrolyzes it into ammonium (NH_4^+) and bicarbonate (HCO_3^-) (Davies et al., 2022). This phenomenon also releases CO_2 and water and increases the pH of the soil, which triggers the volatilization of ammonia (NH_3) under alkaline conditions. This urease hydrolysis is affected by different factors such as temperature, soil moisture, microbes and organic matter (Ni et al., 2022). After the hydrolysis, nitrification occurs in a two step- oxidation process to convert ammonium (NH_4^+) into nitrates (NO_3^-). Initially Nitrosomonas bacteria converts ammonium (NH_4^+) to nitrite (NO_2^-) and finally Nitrobacter bacteria converts nitrite (NO_2^-) into nitrates (NO_3^-). Nitrates are more mobile species as compared to ammonium, and they are mostly leached down in well irrigated soils (Gao et al., 2023).

This leaching of nitrates is the significant cause of Nitrogen loss from the soil and reduces the groundwater quality and NUE. In the soil with high pH conditions, ammonia volatilization occurs when ammonium (NH_4^+) is converted to ammonia gas (NH_3), which is further release in the environment and increases atmospheric nitrogen emissions (Wu et al., 2021). This released ammonia is further converted to nitrous oxide (N_2O), a potent greenhouse gas which has more significant impact than CO_2 in global warming and ozone depletion. The nitrate ions (NO_3^-), leached in the groundwater enters water reservoirs and causes eutrophication, algal blooms and low dissolved oxygen levels, which are harmful for aquatic life (Romanelli et al., 2020).

The consistent use of urea fertilizer deteriorates the soil health profile by reducing the water and nutrient holding capacities, organic matter load, pH and porosity while increasing salinity, pests, eutrophication, acidification and nitrate leaching (Pahalvi et al., 2021). Crops only utilize a very small portion of nitrogen available through urea, the major portion enters air in the form of ammonia, nitrous oxide and its derivatives through volatilization (Skorupka et al., 2021) and remaining leaches to water bodies and aquifers in the form of nitrates, which further impacts aquatic life (Yang et al., 2022). Nitrate contaminated water drinking causes serious human health issues whereas nitrous oxide release in the atmosphere contributes to depleting ozone layer and climate change (Motasim et al., 2024).

In the latest years, zinc deficiency has become a major concern world-wide (Khan et al., 2022). Zn deficiency is present almost all around the world, but it dominates in the calcareous agricultural lands of China, India, Australia, Turkey, Australia and Pakistan (Ahsan et al., 2021). High rates of calcium, phosphorous and organic matter in the soil reduces the availability of Zn to the plants, due to which Zn deficient grain is produced and ultimately cause Zn deficiency in animals and plants (Lakshmi et al., 2021). Zn deficiency in humans may cause serious health problems including respiratory diseases (16%), diarrheal disorders (10%), skin diseases, malaria (18%) anemia, poor physical growth, low immunity levels, cancers, ulcers, adverse pregnancy outcomes (Praharaj et al., 2021) and approximately 800,000 deaths per annum in the poor population of the world (Younas et al., 2023).

Zinc is a key element in the structure of DNA and RNA in both animals and plants, and a significant structural part of proteins and various metabolic and physiological reactions (Cuajungco et al., 2021). It majorly contributes to the synthesis of chlorophyll by activating several enzymes in the synthesis pathway (Mousavi et al., 2024).. It also regulates photosynthesis and ensures the structural integrity of chloroplasts (Rai-Kalal et al., 2021). Zinc also acts as cofactor for the activation of more than 300 enzymes such as carbonic anhydrase and superoxide dismutase which are responsible to regulate the utilization of CO_2 and relieves oxidative stress, respectively (Cao et al., 2020). Zinc also plays an essential role in synthesizing indole-3-acetic acid (IAA), the primary auxin in plants. It also regulates cell elongation and plant growth by facilitating amino acid metabolism (Sourati et al., 2022). An effective method to treat the Zn deficiency in human diet is enriching plants with zinc, ultimately enhancing Zn levels in the whole food chain. Zinc incorporated fertilizer such as Zn-chelates, ZnSO4 and ZnO can be used in this regard. They allow a reduced and steady release of Zn, creating them a better choice (Beig, Niazi, Jahan, et al., 2023).

Zinc chelates such as Zn-EDTA have controlled release of zinc in the soil because of their organic nature which enhances the bioavailability of zinc. This helps in the prolonged availability of zinc to the plants and simultaneously reduces the micronutrient deficiency (Chen et al., 2022). $ZnSO_4$ is commonly used zinc fertilizer which has good solubility, and it releases Zn rapidly for the immediate uptake by plants, which is advantageous for short term agricultural processes, but it also causes the nutrient leaching resulting in zinc loss (Dhaliwal et al., 2022). ZnO is also used as slow-release fertilizer as it is less soluble than $ZnSO_4$. It improves the long-term availability of zinc in soil by releasing it slowly over time, this also reduces the leaching. In calcareous soil, this slow release often causes micronutrient deficiency, and it may require addition of extra zinc supplements (AbdElAziz et al., 2021). Even with their desired benefits, these Zn fertilizers also have some major drawbacks such as high cost and environmental impacts. For example, synthesis of Zn chelates is very expensive, due to which they are not reasonable for small- scale farmers. These fertilizers also contaminate soil and water, if they are not fully absorbed or utilized by plants. Their accumulation in the soil may be toxic and hazardous for soil and ecological factors (Montalvo et al., 2016). As this world is aiming to progress towards environment friendly practices and sustainability, hence these commercially available nutrient supplements such as Zn chelates impose direct impacts on the environment and are rather expensive (Almendros et al., 2024).

Recently, development of fertilizers with controlled release mechanisms and tailored nutrient supply has gained significant attention among the researchers. Initially, urea fertilizers were coated with different types of materials such as inorganic substances to enhance nutrient use efficiency, reduce environmental impacts and increase crop yield (Annapurna et al., 2020). Later, different types of strengthening materials such as starch and adhesives were added to the coatings (Wang et al., 2023) and finally some studies reported the dual coatings of urea fertilizer to achieve two or more agricultural challenges simultaneously (El-Ghamry et al., 2021). They have been thoroughly investigated but it is not substantial, particularly on the ones that release tailored micronutrients. Currently, researchers are focusing on advanced nanotechnology extensively to introduce new controlled-release fertilizers with better performance. Nanotechnology is used to limit the N-losses, reduce chemical uses while simultaneously improving crop output and pest management (Pramanik et al., 2020). Different types of nanomaterials are synthesized for agricultural advantages, they include carbons quantum dots CQDs (Zhu et al., 2022), carbon nanotubes CNTs (Patel et al., 2020), fullerenes (Jha et al., 2023) and carbon fibres (Meraz-Dávila et al., 2021). Among them CQDs have gained the most attention because of their easy synthesis, very small size (less than 10 nm), tunable properties, super-solubility, biocompatibility, negligible toxicity and fluorescence properties (Sun et al., 2022).

1.1.2 Significance:

A few studies have been conducted so far that focus on the effect of CQDs on plant health and overall crop quality. Only one study has been conducted until now that reports the use of CQDs as a carrier of slow release of Zn micronutrient by growing plants with nutrient-CQDs solutions (Beig et al., 2023). Also, many studies reported the usage of different coating materials on the urea fertilizer to slow down its N-release rate such as diatomite (DE), nutrient doped hydroxyapatite (Sharma et al., 2022), nano diatomite (NDE) (Mirbolook et al., 2023) and mostly bio-based polymers.(Tian et al., 2022; Zhang et al., 2022)

In this study for the very first time CQDs specifically Zn doped CQDs, infused in a hydrogel, are coated on urea fertilizer as an outer protective barrier. The inner coating is a thick bio-polyurethane coating synthesized from LCS. The inner layer will be responsible for the slow release of N from urea and the outer coating will tailor the zinc supply for plants, while contributing to the slow-release mechanism through its hydrophobic hydrogel. This layer prolongs nutrient availability to plants by responding to environmental factors such as moisture and temperature, thus aligning nutrient release with crop demand. This formulated dual coating will address two major global issues at the same time; firstly, the excessive release of nitrogen from urea fertilizers that is lost through either volatilization as ammonia in the air or leaching as nitrate compounds in the soil. And, secondly, zinc deficiency in both plants and humans.

1.1.3 Objectives:

The objectives of the study were to:

1. Synthesize and characterize zinc doped carbon quantum dots (Zn-CQDs) by employing hydrothermal technique.
2. Prepare and analyze liquified cotton straw- LCS from dried cotton stick powder to synthesize bio-polyurethane.
3. Develop dual coated urea fertilizer; bio-polyurethane (BPU) as inner coating, and Zn-CQDs infused hydrogel as outer protective coat.
4. Evaluate the cumulative Nitrogen release rate of dual coated urea by using water release test and sand columns testing. Estimate the pattern and concentration of zinc in release tests samples.

CHAPTER-II LITERATURE REVIEW

2.1 LITERATURE REVIEW

2.1.1 NITROGEN LOSS-A global challenge:

Urea is the most popular nitrogen (N) source in the world since it contains nitrogen and costs relatively less. Nevertheless, its application raises major concerns due to huge losses of nitrogen, for example through volatilisation, leaching and denitrification, which causes environmental depletion and reduces nitrogen uptake by crops. This inefficiency is a major problem that resonates around the world, in terms of both agricultural output and the earth's physical condition. Substantial amount of nitrogen in urea is lost through a process known as ammonia **volatilization**. Urea decomposes into ammonium ion in the soil and ammonia gas if the ammonium ion is not absorbed by the plants or is not retained by the soil (Li et al., 2022). This is increased in the areas of high temperatures and alkaline soils since ammonia volatilization is faster in such conditions.

As nitrogen is wasted in the process of volatilization as ammonia, crops are deprived of this vital nutrient and require the addition of more fertilizer for the same yield and as a result the farmer incurs higher costs (Motasim, Samsuri, Nabayi, Akter, Mohammad, et al., 2024). However, nitrogen **leaching,** which is another possible fate of nitrogen fertilizer, have negative effects on agricultural productivity and the environment. The nitrification of urea in the soil produces very mobile nitrates. Nitrates can run-off into the water supply through excess rain or irrigation and contaminate the groundwater aquifers and surface water systems (Wang et al., 2019). This results in the eutrophication of water bodies encouraging the formation of algal blooms, which suffocate water by consuming oxygen and affect aquatic life. Leaching is highly dangerous in areas with sandy soils, and in the soils with higher rates of irrigation because the root zone has low nitrate retention capacity (Martínez-Dalmau et al., 2021). **Denitrification** is another process through which nitrogen is lost, in which nitrates are transformed into gaseous nitrogen gas (N_2) and nitrous oxide (N_2O). Nitrous oxide is responsible for catalysing climate change and stratospheric ozone depletion (Goyal et al., 2023). Denitrification is facilitated by a bacterium in the absence of oxygen, which uses nitrates as electron acceptors to convert them into other forms. Following shows the order of reaction that takes place during denitrification (Oh et al., 2023):

1. Reduction of nitrate (NO_3^-) to nitrite (NO_2^-).
2. Conversion of nitrite to nitric oxide (NO).
3. Reduction of nitric oxide (NO) to nitrous oxide (N_2O).
4. Reduction of nitrous oxide (N_2O) to nitrogen gas (N_2).

These steps are also affected by different environmental factors such as pH of the soil, temperature, moisture and carbon status within the soils. For example, denitrification increases water-filled pore space of soil ranging from 80-95% because oxygen diffusion in the soil reduces and it results in the occurrence of anaerobic micro-site (Highton et al., 2022). Higher concentrations of organic carbon fulfil the energy needs for denitrifying bacteria, the requirements to facilitate the process.

Different soil conditions respond differently in the release of nitrous oxide (N_2O) (Ayiti & Babalola, 2022). Warmer temperatures increase the activity of microbes which further accelerates the rate of denitrification (Dai et al., 2020). Excessive nitrates in the soil provides free substrates for denitrification and increases the production of nitrous oxide (N_2O) (Li et al., 2022). Soil with acidic pH has increased nitrous oxide (N_2O) release as compared to alkaline soils because acidic soils cause incomplete denitrification and alkaline soils causes complete denitrification and results in N_2 (Jun et al., 2024). Soil moisture is also directly proportional to the rate of denitrification. Increased soil moisture causes decrease in oxygen levels and favors denitrification.

Denitrification is maximized at the intermediate moisture levels (Liao et al., 2022). Denitrification is a natural phenomenon in nitrogen cycle but the rate at which this process is accelerated, is because of applying too much urea and poor management of soil. Wet and poorly drained soils, commonly found in rice paddies and some irrigated crops create anaerobic conditions that triggers denitrification, further contributing to nitrogen loss (Timilsina et al., 2020). Urea fertilizers can be inefficient in the above ways due to its importance in food production Security. In many regions especially in the developing countries, the farmers use more urea to make up for the loss of nitrogen through volatilization and leaching hence costing more to produce food. Thus, even if farmers use more fertilizers, they get less output to reflect the use of fertilizers hence reducing profits and increasing poverty among small communities.

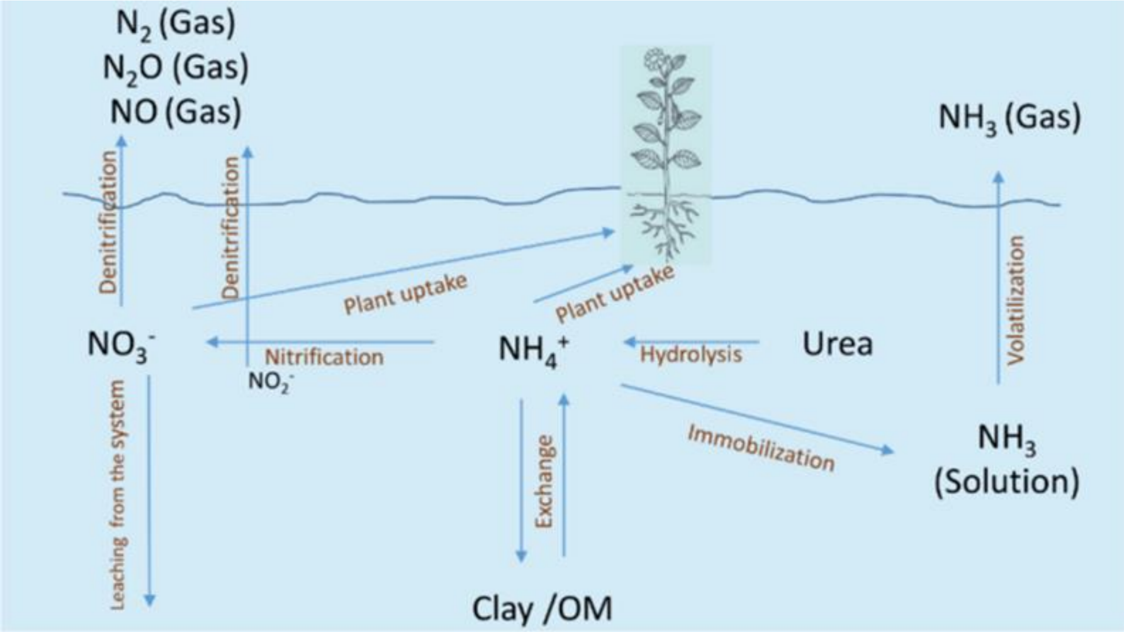

Figure 1: Nitrogen losses occurring in the soil upon the application of urea fertilizer (Motasim et al., 2024) – urea hydrolysing into Ammonium ion (some of it is absorbed by plants and remaining is converted to nitrates) – nitrates are converted to nitrites (nitrification) and a major fraction of them is leached down (leaching) - nitrites are reduced (denitrification) to nitrous oxide and nitrogen gas (volatilisation).

Effects of Nitrogen loss is not confined to soil only, as it is evident from the environmental effects of nitrogen loss to agriculture (Madan et al., 2020). Nitrate concentrations in water sources may make human sick leading to cases of methemoglobinemia better knows as "blue baby syndrome in infants(Choudhary et al., 2022) and other major health problems in adults (Martin et al., 2021). Also, nitrous oxide emission due to denitrification is becoming an issue of major concern in relation to international climate change policies because of their large contribution to global inventories of greenhouse gases (Ramzan et al., 2020).

Therefore, nitrogen loss from urea fertilizers is a real concern for the entire world. The literature shows that it not only reduces the effectiveness of food production systems but also leads to other major environmental concerns such as water pollution, eutrophication and emissions of Green House gases. Solving this problem is complex and calls for the development of the existing fertilizers and overall management of soil in crop production and framed policies regarding the use of Nitrogen in the farming systems.

2.1.2 CARBON QUANTUM DOTS (CQDs)-Introduction and Properties

CQDs were first discovered in 2004 while the purification of single walled carbon nanotubes, where photoluminescent carbon nanoparticles were extracted as a byproduct, (Xu et al., 2004) They are quasi-spherical nanoparticles and have less than 10nm diameter (Aslan et al., 2021). They are a novel class of carbon nanomaterials that have gained significant popularity among researchers because of their tunable properties and favorable applications (Jia et al., 2020). They have exceptional properties such as biocompatibility (Pandiyan et al., 2020), low toxicity, fluorescence, photoluminescence (Zhang, Yang, et al., 2022), optical, electronic and chemical properties (Eskalen, 2020). These properties make them a potential research aspect in the field of bio-imaging, drug delivery, sensing, energy storage, catalysis and many other fields (Khan et al., 2022).

The most attractive property of CQDs is their photoluminescence, ability to emit or absorb light with stability ranging from ultra-violet to Infrared across the spectrum (Hagiwara et al., 2021). This property makes CQDs an important participant in opto-electronics and bio-imaging (Hesari & Ding, 2020). The photostable luminescence property of CQDs is due to their fine size, surface properties and quantum confinement effect, where the electronic properties of a material changes due to their extremely small size (Methods, 2020.). CQDs are super water soluble and less toxic as compared to other nanomaterials, which make them more desirable and environment friendly (Zhao et al., 2021). The introduction of any foreign atom (dopant) into the carbon core structure of CQDs to modify their electronic structure and enhance their properties is known as doping. It improves the optical, electronic and catalytic properties of CQDs and expand their potential applications (John et al., 2021). Most used doping atoms include Nitrogen (N), Sulphur (S), Phosphorous (P), Copper (C), Zinc (Z), Iron (Fe) and Boron (B) (Kou et al., 2020). Doping alters the photophysical properties of CQDs by introducing defective sites and affecting the surface states. These changes induce tuneable light emission and absorption (Dsouza et al., 2021). Some properties of carbon quantum dots (CQDs) can be boosted by doping them with zinc to make them applicable in agriculture. Zinc doping mainly enhances the function of CQDs such as fluorescence, quantum yield, stability and surface reactivity. The introduction of zinc atoms into the carbon lattice results in the change of electronic and optical characteristics of the CQDs (He et al., 2021). This process incorporates new active functional groups that facilitate the flow of electrons, regulates surface interactions and is particularly important in fields such as nutrient sensing and delivery systems of controlled-release fertilizers (Alikhani et al., 2023).

For instance, CQDs doped with zinc have enhanced photoluminescence properties and other improved characteristics when used under various conditions. This is due to the ability of zinc to passivate the surface energy traps to limit the fluorescence quenching and increase the emission intensity. In addition, the chemical and structural stability of the doped CQDs also improves, which is essential for their service life in field conditions (Zhao et al., 2020).

Synthesis techniques for CQDs include top-down approaches such as arc-discharge (Chao-Mujica et al., 2021), laser ablation (Cui et al., 2020) and bottom-up approaches that involve hydrothermal (Lai et al., 2020a), solvothermal (Palacio-Vergara et al., 2023) and microwave pyrolysis(Zhu et al., 2021). All these methods provide different degrees of controlling the size, surface charge of the particles and their quantum yields. These tuneable properties improve their potential in sustainability and advanced applications such as photo catalytical processes and photovoltaics (Rasal et al., 2021). The synthesis of CQDs is generally simple, cost effective, and in many cases environmentally friendly, when a green precursor is used (Manikandan et al., 2022). Moreover, due to their water-soluble and physiologically stable character, they are suitable for applications in biomedical usage such as in drug delivery and tissue imaging(Luo et al., 2020).

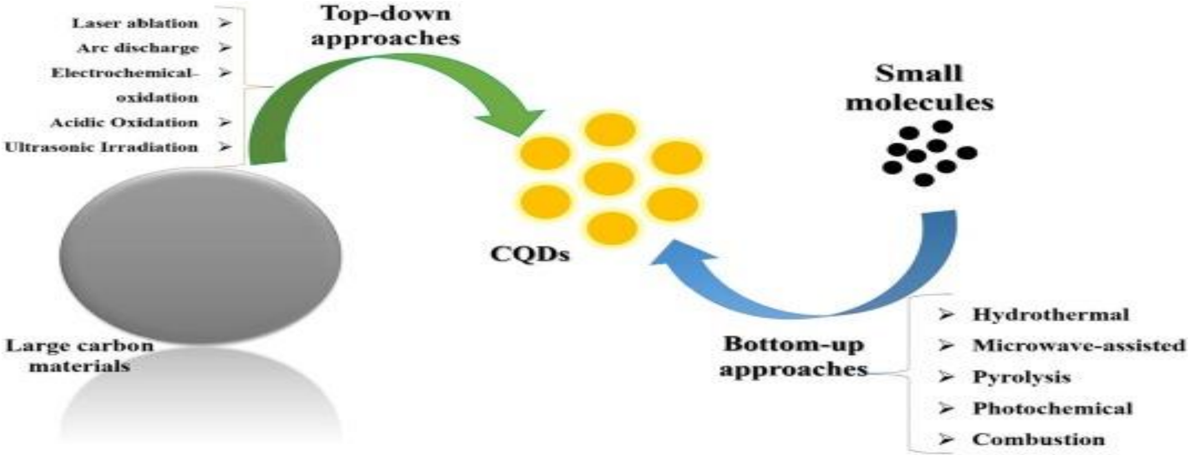

Figure 2: Illustration of Top-Down and Bottom-up synthetic techniques of carbon quantum dots (CQDs) by (Saraswat et al., 2024)- depicting that in top-down approach, a large sized carbon material is reduced into CQDs while in bottom-up approaches, small sized carbon material is combined to synthesize CQDs.

2.1.3 CONTROLLED RELEASE FERTILIZERS- CRFs

The concept of controlled-release fertilizers or CRFs has been developed as a recent innovation in the field of agriculture to overcome deficiencies of the conventional fertilizer use. They have been developed to deliver nutrients to the plant in a slow manner that fulfils the plant’s nutrient requirements throughout a certain period and enhances crop production and simultaneously reduces the impacts on the environment. This slow-release mechanism is achieved by developing coatings or formulations to slow down the solubility rates of the nutrients which include nitrogen, phosphorus and potassium (Vejan et al., 2021).

Another aspect which has greatly supported the use of CRFs is that it has less nutrient loss from leaching, volatilization and denitrification. Chemical fertilisers such as urea or ammonium nitrate makes the nutrients easily available and therefore the losses are also enormous. As for the nutrient that often records high incidences of loss, it is Nitrogen, which losses are attributed to volatilization, a process wherein Nitrogen present in the form of ammonia gas is released to the atmosphere (Ransom Id ¤ et al., 2020). Also, leaching is present where water moves through the soil and nutrients dissolved in the soil also move away from the root zone and cause water pollution. Because nutrient release with the help of CRFs is gradual, the immediate release of the nutrients in the soil is minimized, and nutrient use efficiency is enhanced (Jariwala et al., 2022).

The other benefit of CRFs is that they tend to reduce the frequency of applying fertilizer to the soil. According to the above-mentioned conventional systems, it is expected to use the fertilizers several times so that the crops are provided with nutrients at every time they pass through their development stages. On the other hand, CRFs, in most cases, one application is sufficient since nutrients are released gradually in the plant root zone (Rahman et al., 2021). This not only reduces operating cost, mostly in terms of labour and cost of sourcing manpower but also ensures that the nutrient solution concentration does not accumulate and become toxic to the plant. They are also useful in encouraging more even growth of crops as the controlled-release fertilizers release the nutrients in the appropriate rates and time (Fertahi et al., 2021).

2.1.3.1 Mechanism of CRFs:

Controlled-release characteristics of CRFs are made possible by using coatings or chemical formulations. One such method is the technique of coating the fertilizer granules with a layer of polymer material. Such coatings are formulated in such a way that they degrade progressively over a period depending on parameters such as moisture content in the soil, temperature and microbial action (Moradi et al., 2024). For instance, urea coated with sulfur is an example of a CRF with a layer of sulfur surrounding a urea granule to determine the rate at which it dissolves (Sun et al., 2023). Over time, the sulfur dissolves, creating a pathway for water to enter the granule and dissolve the urea present in it.

Besides sulfur, different items including resin, waxes, starch (Channab et al., 2023)and bio-based polymers have been used as a coating material (Chaudhary et al., 2023). These coatings can be modified to react to the changes in the environment such as the acidity of the soil or the temperature in the soil to make nutrient release more accurate (Mansouri et al., 2023). For example, some of the coatings, such as those that are temperature sensitive may release the nutrients at warmer climate, which is during plant growth, where nutrients are mostly needed (Z. Li et al., 2023).

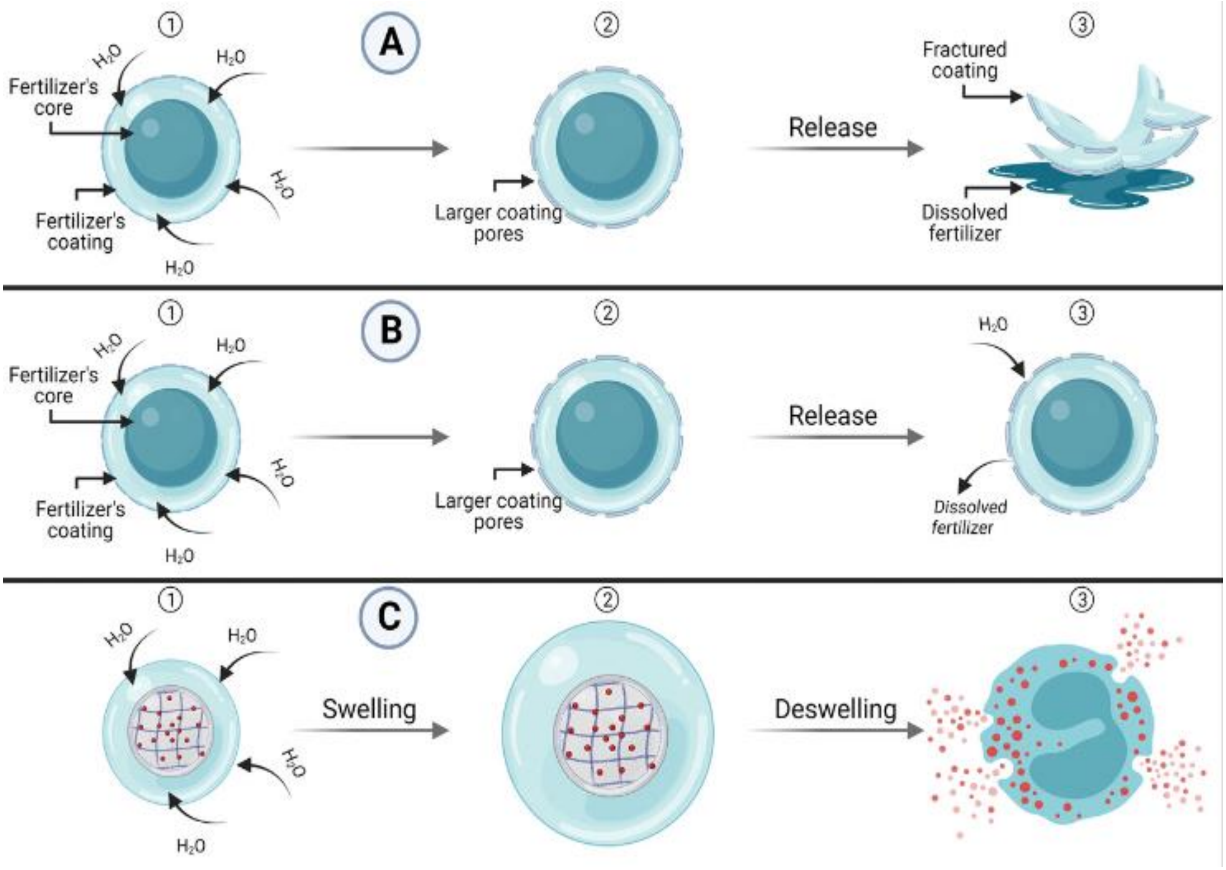

Figure 3*:* by (Mansouri et al., 2023) describes the different possible behaviors of coating material, once they encounter the osmotic pressure of water. **A** depicts the sudden outburst of the coating material, causing sudden release of nutrients. **B** depicts the gradual release of nutrients from the core through the expanding pores caused by the water penetrating the coating and **C** shows the water absorption by the coating, which swells to slowly release the

There are chemical modifications that have been made for fertilizers and they contribute to the controlled-release systems. Hydrogels are also widely used for this purpose. Hydrogels are highly water absorbent materials which can swell with water up to hundreds of times their mass, releasing water gradually. Such moisture-responsive behaviour is particularly relevant for the areas where water supply can significantly vary (Ahmad et al., 2023). The hydrogel coatings can expand under high humidity and release the fertilizer more quickly thus contracts under low relative humidity and delays the nutrient release. Such moisture sensitive behaviour improves nutrient utilisation since nutrients readily available in the right proportion in the root zone, reducing wastage. The biopolymers including the polyacrylamide and other natural biopolymers have been studied with an aim of enhancing the water absorption and slow release on the available fertilizers (Basta et al., 2021).
Sulphur is one of the most popular coating materials which is related to the control of nutrient release. It works by protecting the substrate from penetration by substances and it dissolves through microbial action or the effects of other factors such as temperature and moisture. Sulphur coated fertilizers are commonly used for slow release of nutrients for example nitrogen from urea (Zhao et al., 2020). The release rate can be varied depending on the conditions of the environment such as pH of the soil that preferentially enhances breakdown of sulphur. This property assists in minimizing Nitrogen losses through Volatilization particularly under alkaline conditions (Ghumman et al., 2022).

Starch or cellulose-based polymers are currently acknowledged as green coating materials because of their ability to replace conventional polymers used in coating systems. They are environmentally friendly and respond to the environmental factors especially moisture and temperature (Firmanda et al., 2022). Bio-based polymers used with encapsulating nutrients for soil application can control the release of nutrients to the plants and have the additional benefit of avoiding leaching in the soil. Also, these materials have a lesser emission ratio than synthetic polymers, making them suitable for use in CRFs (Chaudhary et al., 2023). Some CRFs contain inhibitors that reduce the rates of certain nutrient transformation reactions in the soil. For instance, nitrification inhibitors can delay the process of change of ammonium to nitrate which is likely for leaching (Yaru et al., 2023). Meanwhile, urease inhibitors may slow the process of converting urea to ammonia, thus minimizing nitrogen loss due to volatilization (Freitas et al., 2023).

2.1.4 GLOBAL MICRONUTRIENT DEFECIENCY: ZINC

Zinc is an important microelement for plant and human nutrition. The lack of Zn is a global problem with the consequences that relate directly to the yields of the farming industry and the quality of human life (Kumar et al., 2022). However, according to the literature, identifying the zones of zinc deficiency, more than half of the world's total agricultural lands are deprived of zinc, and nearly two billion people around the globe suffer zinc deficiency, and this problem is especially acute in developing countries (Gupta et al., 2020). The implications are severe and impact food security, human nutrition, and the global economy. Making sure that adequate levels of zinc is available is important in raising yields on crops, health of the population and food security (Praharaj et al., 2021).

2.1.4.1 Role of Zinc in Plant Nutrition

Zinc is an important micronutrient which takes part in many physiological and biochemical processes in plants. It is required for manufacturing of several enzymes; therefore, has importance in protein synthesis, hormone synthesis and stability of cellular membranes. Zinc also plays a role in the synthesis of chlorophyll and the process of photosynthesis (Natasha et al.,2022).When plants lack Zn, their growth is reduced and their leaves turn yellow due to lack of chlorophyll production (chlorosis), apart from being more sensitive to unfavourable conditions such as drought and diseases.(Stanton et al., 2022)

In many plants Zinc acts as part of structure in the enzyme carbonic anhydrase, which plays a significant role in the fixation of carbon dioxide during photosynthesis (Melo et al., 2024). Zinc also takes part in the process of carbon fixation by regulating the conversion of CO_2 to bicarbonate, enhancing photosynthesis. Zinc also contributes to the proper functionality of a wide array of proteins, and it also maintains the integrity of chloroplast membranes that are central for the proper functioning of photosynthetic pathway, particularly under oxidative stress (Han et al., 2021).

In plants, zinc is responsible for the activation of more than three hundred enzymes. These enzymes take part in important cellular activities such as biosynthesis of proteins, carbohydrates and nucleic acids synthesis (Lin et al., 2024). Particularly zinc functions as an activator/cofactor of alcohol dehydrogenase, superoxide dismutase and ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO), they are involved in stress response, antioxidant defence and photosynthesis enzymes, respectively (Hassan et al., 2020).

Zinc also aids the processes of cell elongation and cell division by regulating different plant hormones such as gibberellins and auxins (Hussein et al., 2021). Effect of zinc on root and shoot growth, flowering and overall development of the plant is controlled through changes in hormone concentrations. A deficiency of Zinc results in short stature, chlorosis and weak root system.

Zinc deficiency is most frequent in calcareous soils with high pH usually in arid and semi arid climatic conditions. In such soils, Zn precipitates forming insoluble compounds in water thus limiting the chances of the Zn to be absorbed by plants. This deficiency is more common in large producers of agricultural products in Asian, African and Latin American countries and especially in the crops of rice, wheat and maize (S. Khan et al., 2022). Yield and nutritional value of crops that are exposed to zinc deficiency are low and this further trigger food security challenges in these regions (Hamzah Saleem et al., 2022).

The presence of zinc in plants is not only limited to chemical reactions and growth but also to reproductive maturation. Lack of zinc slows down flowering and fruiting, reducing crop yields (Suganya et al., 2020). Most plants cultivated in soil with low levels of zinc have underdeveloped roots, which makes it difficult for them to absorb water and other nutrients including zinc leading to lower yields and poor quality.

2.1.4.2 Zinc's Role in Human Health

Like all essential nutrients, Zn is required for human life and involves in over 300 biochemical processes within the human body such as DNA synthesis, cell division, immune function and wound healing (Chasapis et al., 2020). It is also important for proteins and carbohydrates’ metabolism. Zinc is also essential in normal growth and development of foetus during pregnancy, infancy and childhood hence it enhances child survival (Nasiadek et al., 2020).

Zinc deficiency in humans is a major health concern specifically in the developing world where most people take cereals and legumes that are low in Zn (Liao et al., 2022). It is evident that zinc deficiency is prevalent in South Asian and sub-Saharan Africa region (Dembedza et al., 2023). WHO estimates that zinc deficiency is cause of more than 800,000 child mortalities every year due to its effect on the immune system, which leads to increased chance of diseases such as diarrhea and pneumonia.

Deficiency of Zn leads to growth failure, delayed puberty, skin rashes, and poor neuro-behavioural development. In pregnant women, Zn deficiency causes preterm delivery and low birth weight and, in young children it increases morbidity and mortality rates (LI et al., 2024).

Zinc is an important micronutrient in both human and plant nutrition, and Global zinc deficiency is a problem that can be solved by biofortification. In agriculture, biofortification is defined as the technique used to enhance the nutrient density of crops, either by breeding or using other agronomic means, including fertilizers (Stanton et al., 2022). Biofortification of zinc is vital to enhance bioavailability of zinc in human diet in regions where people depend on staples that contain low bioavailable zinc like rice, wheat, or maize. Biofortification especially in crops containing zinc has the potential to increase the nutrient density of Zinc and can solve the problem of Zinc deficiency where diet diversity is a major challenge (Stangoulis et al., 2022). Zinc biofortification in agriculture can be done through variety of improvements which increases the concentration of zinc in plants for human and livestock consumption, or through application of zinc such as zinc fertilisation (Younas et al., 2023). The application of zinc to crops by zinc containing fertilizers has been discovered to enhance the availability of zinc in food. For instance, foliar sprays of zinc have resulted to improved uptake of zinc in food crops like rice, wheat and maize crops (Zulfiqar et al., 2021).

Regarding foods fortified with bioavailable zinc, biofortification initiatives have shown that increased availability of zinc in populations consuming these crops would cause enhanced public health (Ramzan et al., 2020). Research indicates that increasing the intake of biofortified staple crops may enhance zinc consumption in the tropics, where the problem of zinc-deficient diets is most apparent. This can lower the likelihood of likely health consequences of zinc deficiency including poor cognitive development, poor immunity, and slow wound healing. In addition, biofortification is another model to enhancing human nutrition and food security by being cheaper and less hazardous to food systems than supplementation programs (Stiles et al., 2024).

CHAPTER-III METHODOLOGY

3.1 METHODOLOGY

The experimental setup followed for this study is illustrated in figure 4. It explains that methodology for this study is divided into three phases, followed by their respective sub-phases.

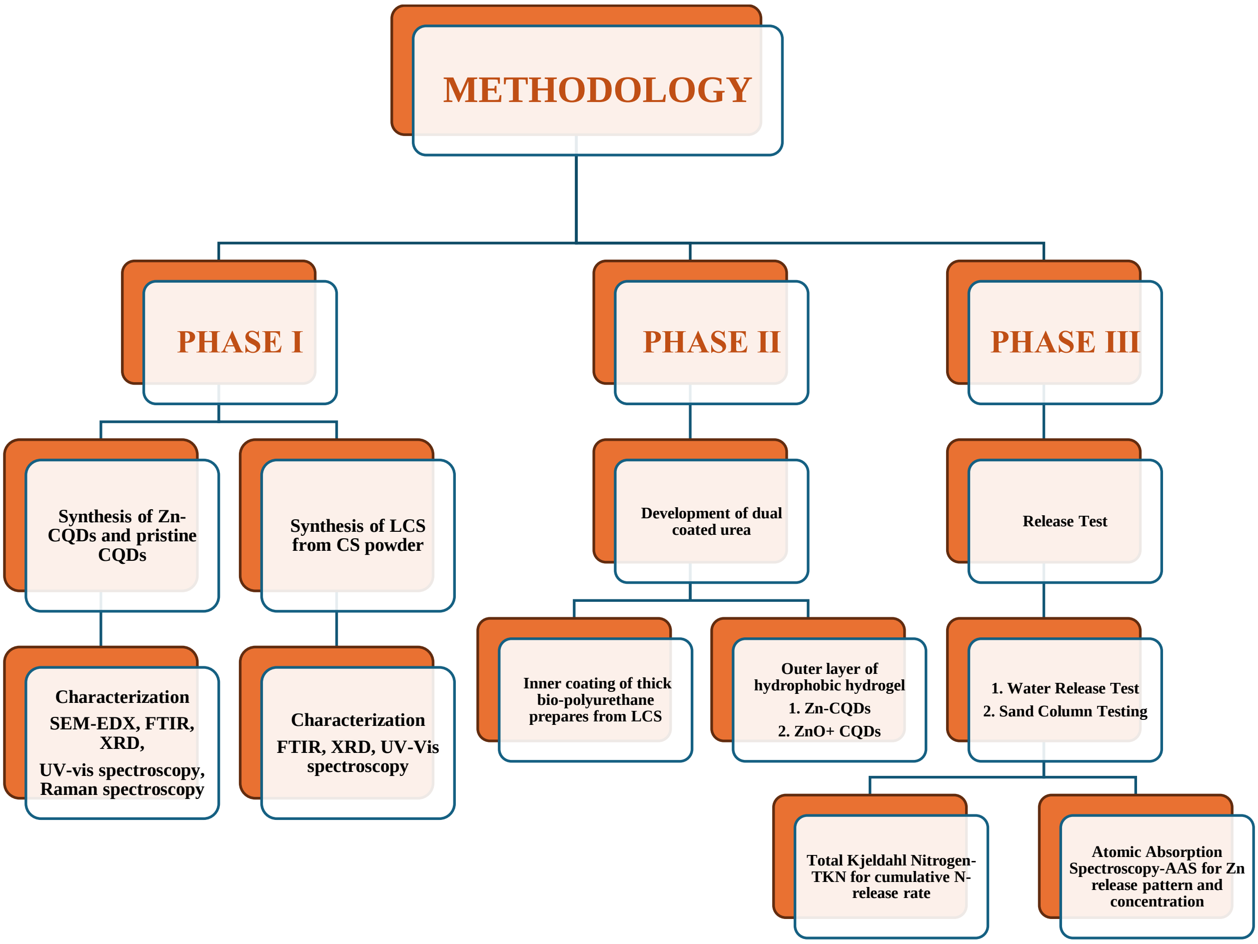

FIGURE 4: Illustration of work order and plan for the research study; Phase I follows the synthesis of ZnCQDs, CQDs and LCS, and their respective characterizations. Phase II follows the development of dual coated urea fertilizer, inner and outer coatings. Phase III follows the release testing of nitrogen and zinc of dual coated urea fertilizer.

3.1.1 Materials and methods:

The research was designed to be conducted in three phases. Phase I included the synthesis and characterization of Zn doped carbon quantum dots and pure CQDS (for control purpose). And the synthesis and analysis of liquified cotton straw (LCS) from dried cotton straw-CS. It was further used for the preparation of bio polyurethane. Phase II included the development and analysis of dual coating on urea. The inner coating is a thick layer of bio-polyurethane, and the outer coating is a protective barrier of Zn-CQDs infused hydrophobic hydrogel. In phase III, first water release test and sand column testing of dual coated urea was conducted and later the samples collected were analyzed for cumulative N content and Zn release concentrations and pattern.

3.1.2 PHASE I

3.1.2.1 Synthesis of Zn-doped CQDs:

Zn-CQDs were synthesized by employing hydrothermal techniques reported by (Alikhani et al., 2023). The following steps were followed; 4.2g of 0.01 mol citric acid and 2.1g zinc nitrate was dissolved in 60 mL of DI with 10-min stirring at room temperature. Transfer the solution to 100ml stainless steel reactor with teflon liner for the immediate hydrothermal reaction at 180 °C for 6 h. After cooling, store the solution in a glass container in a refrigerator. Repeat the whole process until 300ml of raw solution of CQDs is obtained. Dry this solution in oven at 60°C for 24hrs until a powder is obtained. Mix this powder in 1000ml of DI water and sonicate it for 30 mins. Centrifuge the sample at 6000 rpm for 45 minutes. Collect the supernatant and centrifuge it again at 6000 rpm for 45 minutes and again collect the supernatant. Transfer the supernatant to a filtration assembly (0.22µm filter paper), collecting filtrate. Dry the filtrate in oven at 80 °C-90 °C until a powder is formed.

3.1.2.2 Synthesis of pristine CQDs:

CQDs were synthesized by employing the same methodology used for the synthesis of Zn-CQDs. But for pristine CQDs, precursors were different. 4.2g of 0.01 mol citric acid and 2.1g urea were taken as precursors (Lai et al., 2020).

Zn-CQDs and CQDs characterization:

SEM-EDX, FTIR, UV-visible spectroscopy, XRD, RAMAN spectroscopy was used to determine the surface morphology and elemental composition, to identify the molecular composition and functional groups, to determine its concentration and electronic transitions, to determine the crystalline structure and phase identification, molecular vibrations and chemical compositions, respectively to characterize Zn-CQDs.

3.1.2.3 Synthesis of LCS:

The LCS was synthesized by following the procedure described by (Ma et al., 2018). The reaction of liquifying CS powder was done in a 1000 mL three neck flask installed with reflux condenser, thermometer, and motor operated stirrer. 360 g PEG-400, 40 g glycerol and 12 g sulfuric acid were reacted in the three-necked flask with constant stirring. The flask was heated to 160 °C and 80 g CS powder was poured into the flask and reacted with the solvents and stirred continuously. The CS powder was fully degraded after 90 mins and a black liquid was left behind.The flask was then removed and cooled to room temperature to finish the liquefaction reaction.

LCS analysis:

FTIR was used to identify the molecular composition and functional groups, and GC-MS was used for separation, identification, and quantification of chemical compounds specifically -OH groups in LCS.

3.1.3 PHASE II

3.1.3.1 Preparation of dual coated urea

INNER COATING:

Urea was coated in a heating drum roller machine through the following steps: Urea granules were taken in the rotating heating drum machine and preheated at 75 ± 5 °C for 10–20 mins. Then 7% of the thick coating material i.e., bio-polyurethane, which included PAPI (NCO), polyether, LCS (OH), and siloxane with the ratios (n(NCO): n(OH): n(polyether): n(siloxane) = 1: 0.5: 0.5: 0.2) was prepared. The mixture was dropped onto the surface of the rotating urea granules in seven increments. After each increment (layer), urea granules were allowed to roll in machine freely for 10-15 minutes to complete the heat curing reaction. After all the seven layers and heat curing, urea was left to rest at room temperature for a few hours (Ma et al., 2023).

OUTER COATING:

Zn-CQDs

Bio-polyurethane coated urea was further coated with an outer layer by following steps: 0.1 g of Zn-CQDS was dissolved in 10 mL of distilled water and 0.3 g of sodium alginate was added. The solution was mixed using magnetic stirring until it was completely dissolved. The Zn-CQDS + sodium alginate suspension was then sonicated for 15 mins. After that, the copper sulfate solution (0.2 mol/L) was first sprayed into the drum, then Zn-CQDS + sodium alginate suspension was then dropped slowly into the surface of rotating fertilizer granules to form the hydrogel as the outer. The outer coating of hydrogel was formed under continuous rotation of 10 mins to complete the hydrogel crosslinking reaction. Finally, the coated fertilizer was collected and dried in the air.

CQDs + ZnO

Bio-polyurethane coated urea was further coated with an outer layer by following the same methodology as employed for coating Zn-CQDs hydrogel coating, only additional ZnO was taken for CQDs + ZnO hydrogel coating. 0.1 g of CQDS and 0.25g of ZnO were taken for the coating formulation.

3.1.3.4 Coating characterization:

Scanning Electron microscopy SEM was performed to ensure the uniform and successful coating of bio polyurethane on urea granules. It also allowed us to measure the coating thickness around the granules. FTIR was also performed to identify the desired functional groups in the coating matrix,

3.1.3.5 Coated urea granule analysis:

Scanning Electron microscopy SEM was performed to ensure the uniform and successful coating of bio polyurethane on urea granules. It also allowed us to measure the coating thickness around the granules.

3.1.4 PHASE III

Phase III included the water release tests and sand column testing of dual coated urea. The samples collected were analyzed for cumulative N content and Zn release concentrations and pattern.

3.1.4.1 RELEASE TESTS

Water Release Tests:

For assessing the release of dual coated urea fertilizer in water the following method was used, as proposed by (ISO (18644-2016)) standards for controlled release fertilizers: 10g of coated fertilizer was taken in a nylon bag and it was dispersed in 250ml of DI water in a glass reagent bottle. The bottle was kept at 25°C. The bag was shifted to a new bottle with 200ml DI water every 24 hours. The water from the previous bottle is kept for further analysis. This step was repeated daily, and samples were stored. The sampling was done on alternate days for 30 days. Water testing was performed for all i.e., bio-polyurethane coated urea, dual coated urea Zn-CQDs, dual coated urea CQDs + ZnO and untreated urea, for control purposes.

Figure 5: Water release test of urea, BPU and DCRFs at 25°C according to (ISO (18644-2016)). A nylon bag containing the fertilizer, suspended in 200ml of DI water to assess the release patterns of nitrogen and zinc

Sand column testing:

Coated fertilizer's release behavior was also assessed in sand columns by the following steps (Fachini et al., 2022): Sand columns were prepared in 12inches long and 5.5cm wide PVC pipes filled with sand (0-10inch), with a perforated funnel at the lower end for the collection of samples. First 7 inches of the washed sand was placed in the column then 10g of the coated fertilizer was placed and remaining 3 inches of sand was placed. 200ml of DI water was allowed to pass from the top of the column and it was collected from the end of the column, through perforated funnels. The sampling was done on alternate days for 30 days. Samples were collected and stored in separate bottles for further analysis. Sand column testing was performed for all i.e., bio-polyurethane coated urea, dual coated urea Zn-CQDs, dual coated urea CQDs + ZnO and untreated urea, for control purposes.

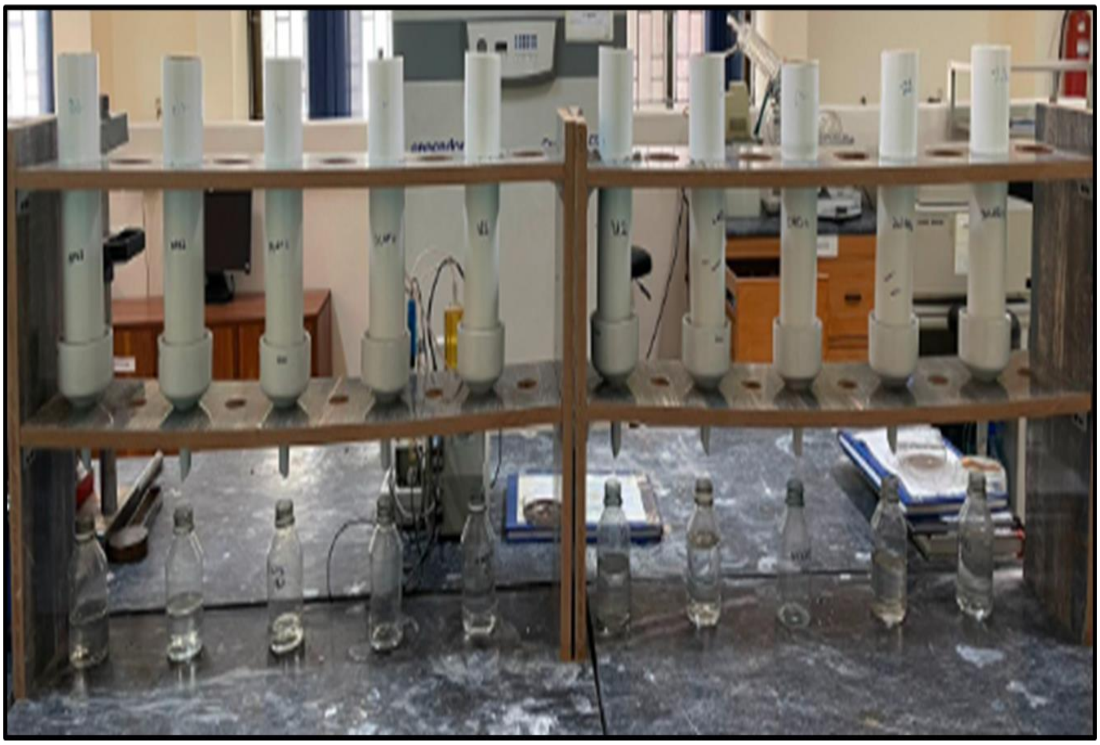

FIGURE 6: Sand column testing of urea, BPU and DCRFs as reported by (Fachini et al., 2022) – fertilizers were kept between the layers of washed sand and 200ml DI water is passes through it on daily basis and the leachate is assessed for nitrogen and zinc release concentrations.

3.1.4.2 Sample Analysis:

a) Total Kjeldahl Nitrogen- TKN:

Protocol to determine total nitrogen (TKN) reported by (Fachini et al., 2022) was such that 10ml of sample was added into cleaned digestion tubes, followed by addition of 0.1 g Copper Sulphate ($CuSO_4$), 3 g Potassium Sulphate (K_2SO_4), 20 ml concentrated H_2SO_4. The digestion of the sample was carried out in DK-6 heating digester (VELP Scientifica, Italy). The digested sample was subjected to distillation in UDK-129 distillation unit (VELP Scientifica, Italy) with 40% NaOH and 4% boric acid solutions. The distillate collected in beaker was then titrated against 1.23 N HCL after adding 6-7 drops of mixed indicator in it. The volume of HCL used was measured and the values were added in formula to calculate the total TKN value. Nitrogen release rate was calculated for all the samples of both water release test and sand column testing in percentage %. Cumulative N release of each product was calculated by adding the individual N% of each sample.

b) Atomic absorption spectroscopy:

Atomic absorption spectroscopy-AAS as reported by (Kurniawati et al., 2021) was used to determine the concentration and release patterns of zinc from all the samples collected through the water release tests and sand column testing of coated fertilizers. All the samples were filtered properly to remove any suspended particle. The digestion of the samples was not required as there was no organic component in the sample. Further dilutions were also not performed as the samples were already super diluted.

CHAPTER IV RESULTS AND DISCUSSION

4.1 RESULTS AND DISCUSSIONS

4.1.1 PHASE I-Characterization of Zn-CQDs:

Following analysis were performed to characterize Zn-CQDs properly:

1. Fourier-transform infrared spectroscopy

The FTIR spectrum of the Zn-CQDs sample was taken to study the chemical structure, type of bonds and functional groups.

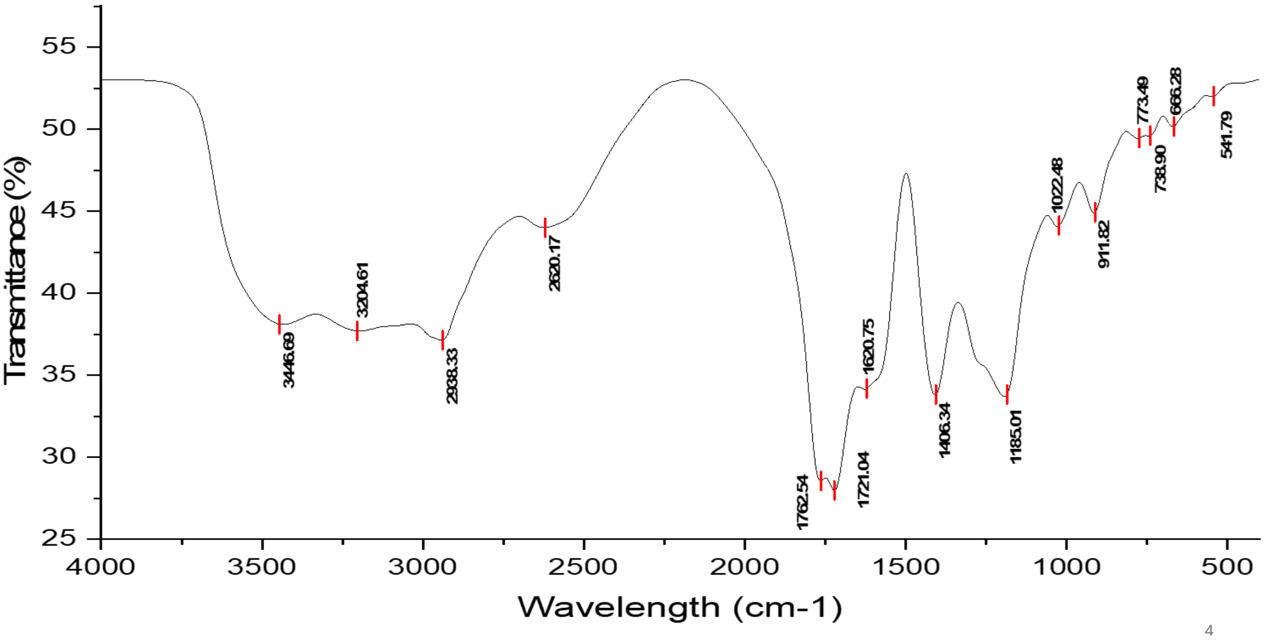

Figure 7: Fourier-transform infrared spectroscopy- FTIR spectrum of ZnCQDs – identifying the key functional groups of ZnCQDs i.e., OH, NH_2, C=O, C=N, C-N and Zn–O.

The peaks at 3446, 3204, and 2938 cm-1 correspond to hydroxyl group stretching vibrations (ν-OH), asymmetric amine stretching vibrations (ν-asym-NH_2), and asymmetric stretching vibrations (νasym CH2), respectively. The peaks in 1762, 1620, and 1185 cm−1 confirm the presence of functional groups C=O, C=N, and C-N. The peak at 699 cm−1 indicates the connection of zinc atoms to CQDs through the Zn–O bond.

The obtained spectrum of the Zn-CQDs was matched with the characteristic peaks reviewed in the literature (Alikhani et al., 2023) as follows: peaks at 3429cm-1 corresponds to hydroxyl group stretching vibrations (ν OH), 3216cm-1 to asymmetrical amine stretching vibrations (ν-asym-NH2) and 2985cm-1 corresponds to asymmetric stretching vibrations (v-asym-CH2). The peaks at 1765cm-1, 1622cm-1 and 1138cm-1 confirm the presence of functional groups C- -O, C- -N, and C- -N, respectively. The peak at 690cm-1 corresponds to the link of zinc metal to CQDs via Zn-O bond. Peaks in the same range with these results were also reported by (Atchudan et al., 2020)

2. X-ray diffraction

The XRD spectrum of the Zn-CQDs was taken to study and determine the crystalline structure and phase identification of sample.

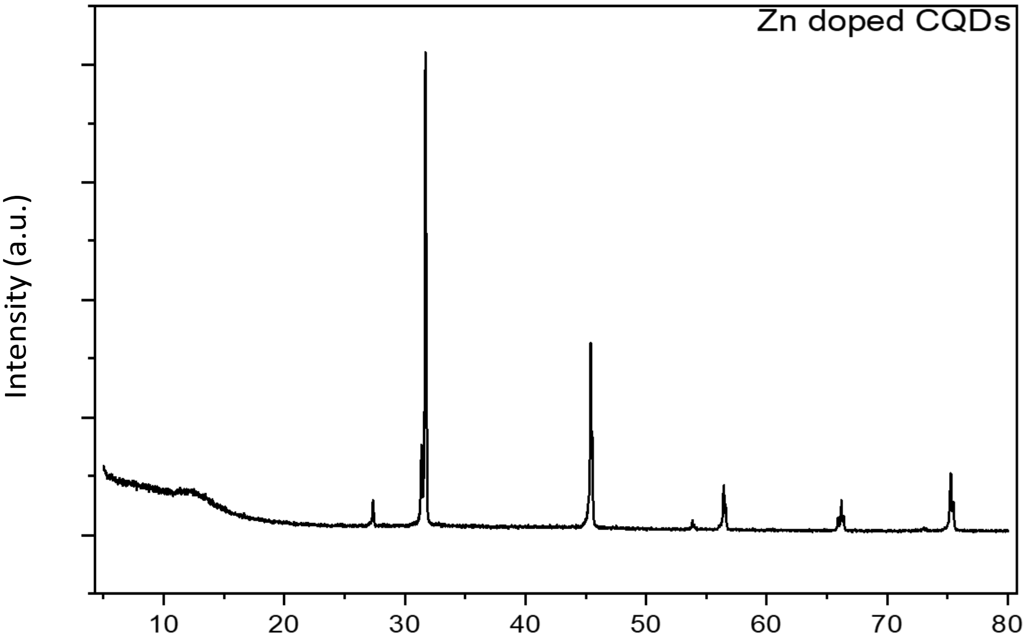

Figure 8: XRD spectrum of ZnCQDs – identifying the planes and structure of ZnCQDs

XRD peaks between 30° to 32° corresponds to the (002) plane of crystalline graphitic layers and (100) plane of ZnO, indicating the successful zinc doping with CQDs. Peaks at 45°, 57° and 66° correspond to the (102), (110) and (112) planes of crystalline graphitic structure. All these diffraction peaks match the crystal planes are associated with the standard ZnO data (JCPDS ref no. 36-1451) (Widiyandari et al., 2023). The same XRD results with the above-mentioned diffraction peaks and planes were also reported (Zhou et al., 2024).

3. UV-Visible spectroscopy

The UV-Visible spectroscopy spectrum of the Zn-CQDs was taken to study and determine the concentration and electronic transitions of the sample.

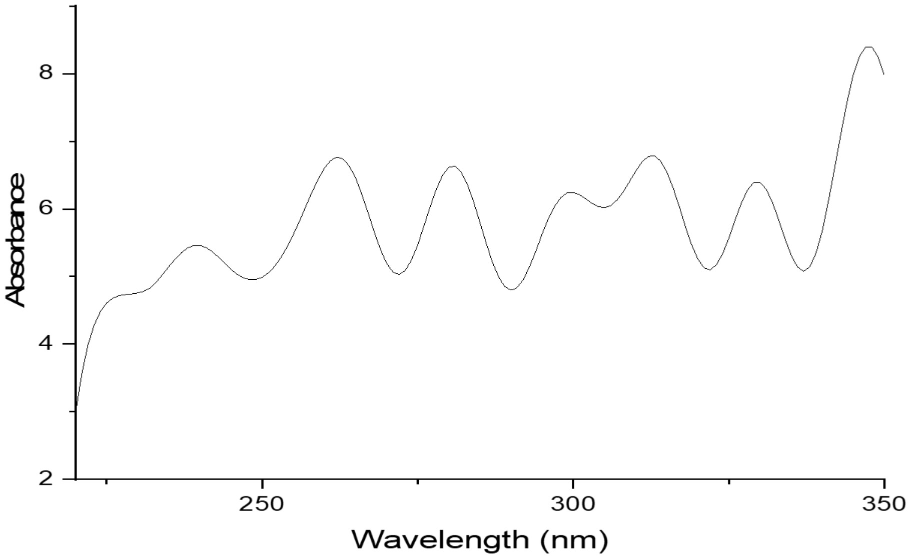

Figure 9: UV-visible spectrum of ZnCQDs – indicating the concentrations and electronic transitions of ZnCQDs

The main peak at 280 nm and a weak shoulder after 360 nm was observed in the UV–Visible spectrum, which are related to π→π* transitions of sp2 aromatic carbons and n→π* transitions of nitrogen or carbonyl groups in Zn-CQDs, respectively. Same results of UV-Visible spectrum were interpreted and reported by (Atchudan et al., 2020)

4. Scanning Electron Microscopy

The SEM of the Zn-CQDs was taken to determine the surface morphology and size distribution of the particles. SEM image showed the spherical structures of Zn-CQDs. It also confirmed that Zn was well attached to carbon nano dots. A study also reported the same morphology of Zn-CQDs (Alikhani et al., 2023). SEM image is as follow:

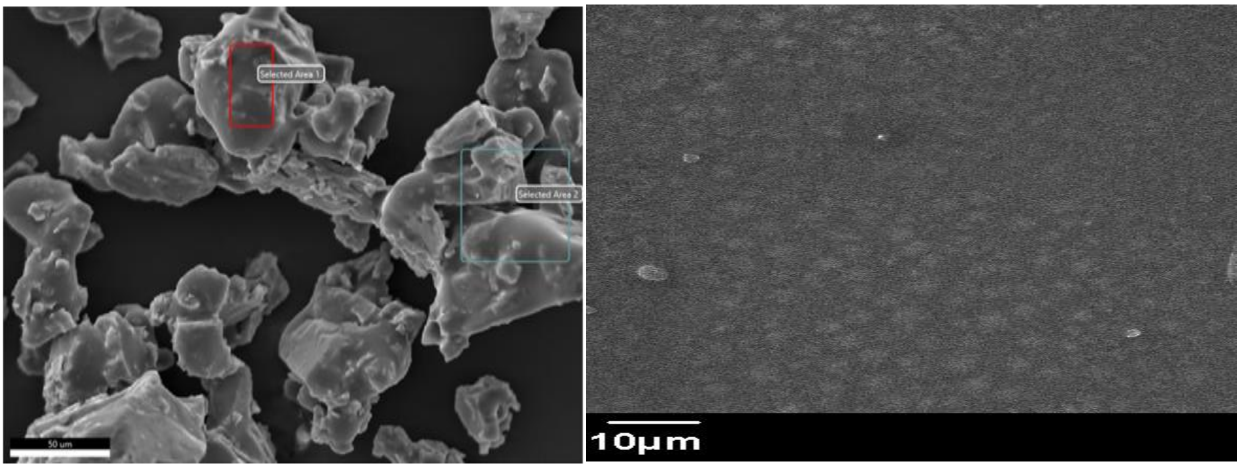

Figure 10: Scanning electron microscopy- SEM images of ZnCQDs depicting the perfect binding of zinc particles with carbon structures.

5. Energy Dispersive X-Ray Spectroscopy

The EDX of the Zn-CQDs was performed to determine elemental composition of the sample and following results were observed:

Table 1: EDX- identifying the elemental composition of ZnCQDs and weight percentage of each element.

ELEMENT	WEIGHT%	MDL	ATOMIC %	ERROR %
C	59.5	0.33	73.9	10.9
O	14.2	0.14	13.3	10.9
Na	10.1	0.11	6.5	8.0
Cl	13.2	0.03	5.6	2.5
Zn	3.0	0.12	0.7	3.8

EDX analysis was performed to ensure the chemical composition and binding of zinc on carbon dots (CDs). The presence and percentages of carbon, sodium, oxygen, and zinc elements in the structure were also determined. Another study reported the same EDX analysis of Zn-CQDs (Alikhani et al., 2023).

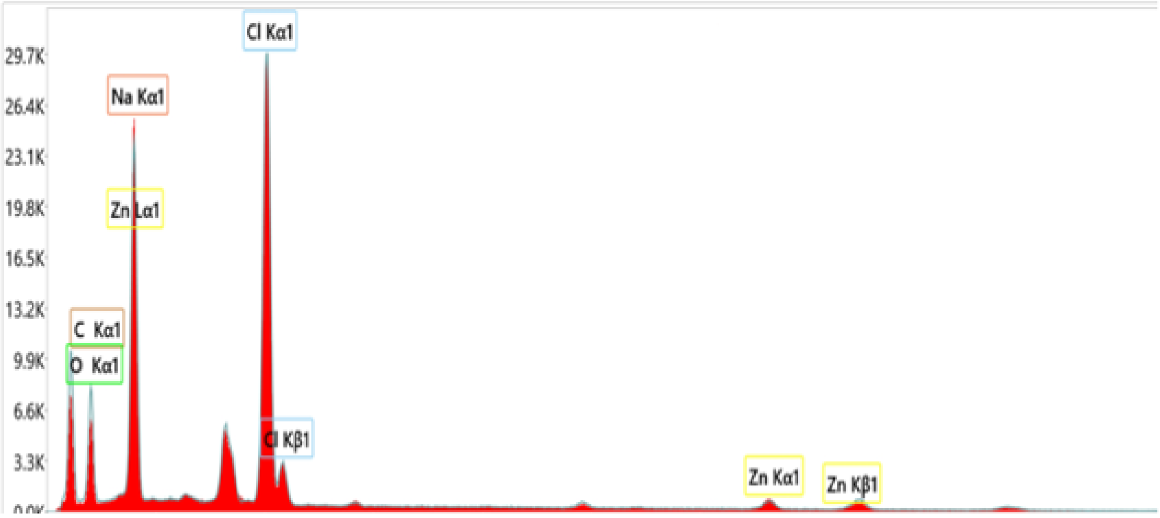

Figure 11: EDX spectrum of ZnCQDs- indicating the respective peaks of each element identified in the EDX analysis.

6. Particle size analyzer

Analysis on particle size analyzer was also performed to confirm the size distribution range of Zn-CQDs. The range of the analyzer was 12nm onwards. No particle was detected by the machine, which confirmed that all the particles were less than 12nm.

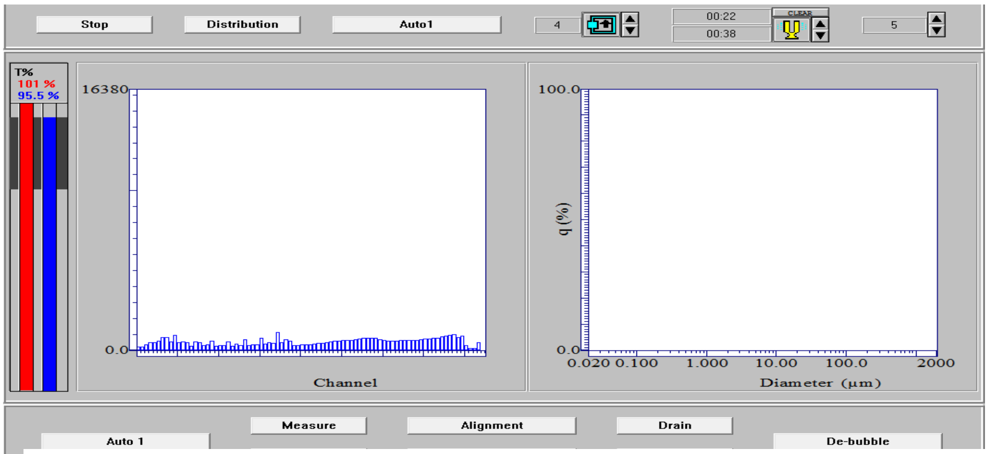

Figure 12: Particle size analyzer- ZnCQDs were not detected by it confirming that its size was less than 10nm because the range of particle size analyzer was greater than 10nm.

4.1.2 Characterization of Pristine CQDs:

Following analysis were performed to characterize CQDs properly:

1. Fourier-transform infrared spectroscopy

The FTIR spectrum of the CQDs sample was taken to study the chemical structure, type of bonds functional groups.

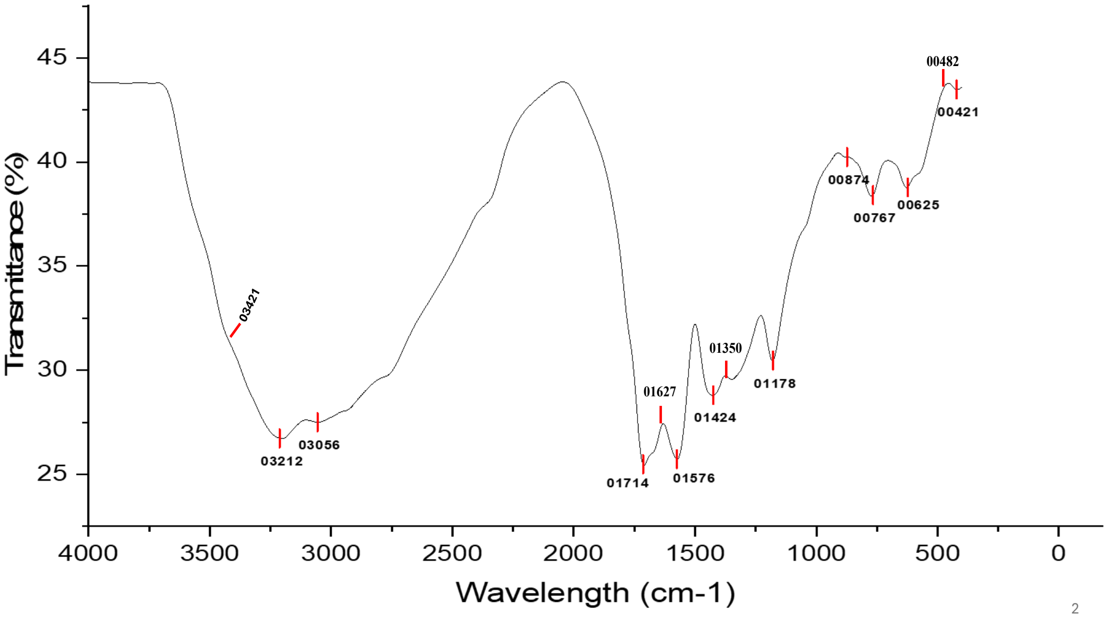

Figure 13: Fourier-transform infrared spectroscopy- FTIR spectrum of CQDs identifying the key functional groups of CQDs i.e., OH, C=O, C=N, C-N and C-C ¼ O.

The peak at 3421cm-1 corresponds to the -OH group and the peak at 1627cm-1 belongs to the stretching vibration absorption peak of C ¼ O. The peak at 1350cm-1 is because of stretching vibration peak of C- -N. The peak at 480cm-1 is due to plane deformation vibration of C-C ¼ O.

The labelled peaks in the spectrum were compared to the characteristic peaks reported by (Lai et al., 2020). Peak at 3412cm-1 belongs to the -OH group of adsorbed water, peak at 1624cm-1 corresponds to the stretching vibration of C ¼ O. The peak at 1342cm-1 is assigned to stretching vibration of C- -N, while the peak at 520cm-1 is in plane deformation vibration of C-C ¼ O.

2. X-ray diffraction

The XRD spectrum of the CQDs was taken to study and determine the crystalline structure and phase identification of sample.

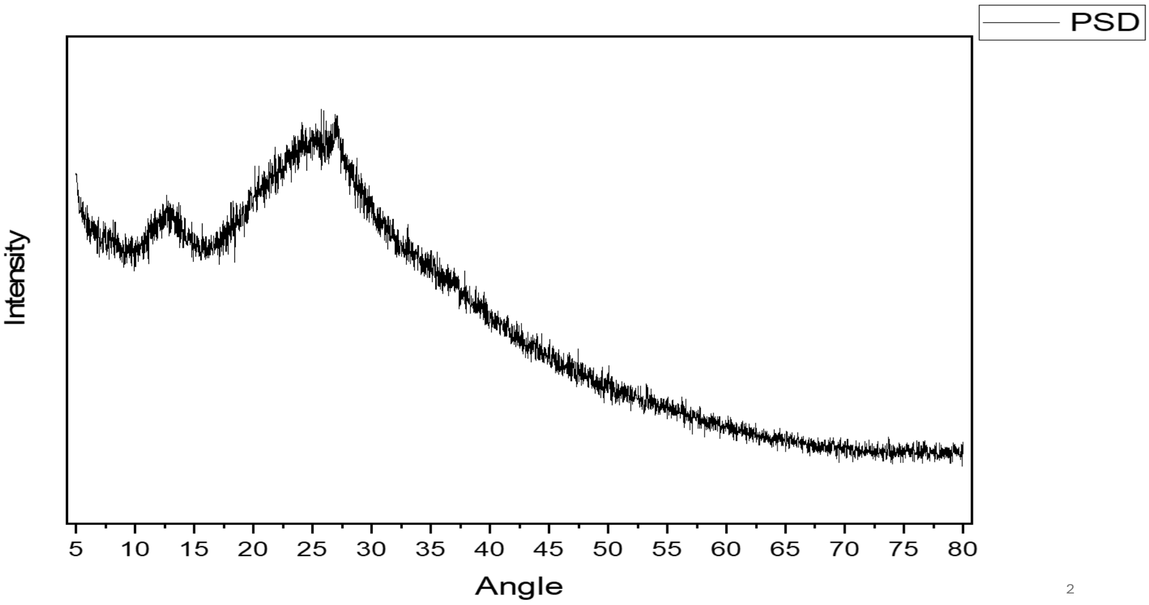

Figure 14: XRD signal of CQDS - identifying the planes and structure of CQDs

The amorphous phase of CQDs is shown by the broad peak of XRD pattern. The top peak at 25 degrees belong to the (002) planes of graphene carbon. This peak indicates the presence of graphitic domains within the carbon quantum dots, which is a common characteristic of CQDs. It can be concluded that a little amount of N would not affect the intrinsical structure of CQDs. Same type of XRD pattern was reported by (Lai et al., 2020b), where broad peaks at almost 25 degrees corresponds to (002) planes of graphene carbon.

3. UV-Visible spectroscopy

The UV-Visible spectroscopy spectrum of the CQDs was taken to study and determine the concentration and electronic transitions of the sample.

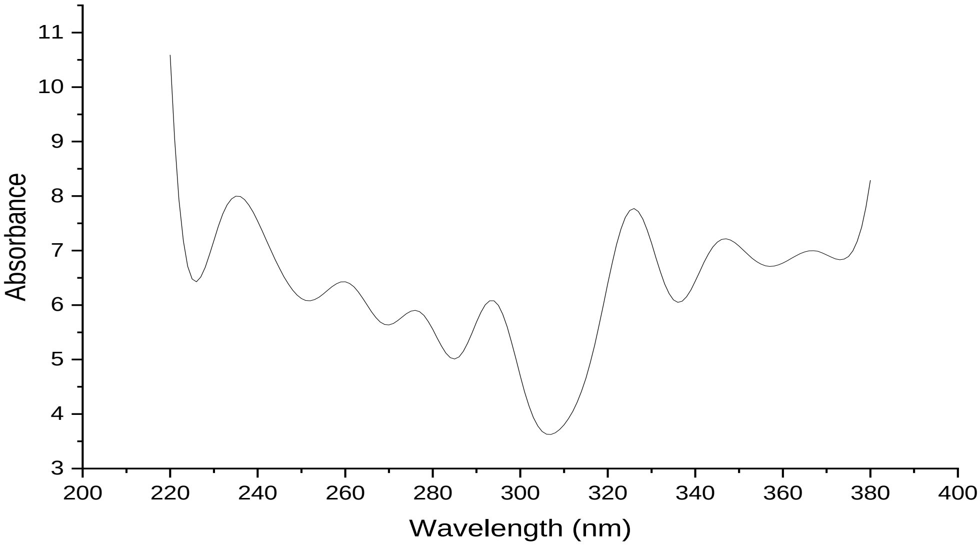

Figure 15: UV-visible spectrum of CQDS - indicating the concentrations and electronic transitions of ZnCQDs

The absorption spectrum of CQDs showed two significant peaks i.e., 240nm and 330nm. The peak at 240nm corresponds to the π–π∗ transition of conjugated C=C bonds of aromatic sp2 domain and the peak at 330nm is due to n-π* transitions, typically originating from the carbonyl (C=O) groups or other oxygen-containing functional groups.

The obtained spectrum of CQDs was matched with the characteristic peaks reviewed in the literature. The peak at 240nm is ascribed to the π–π∗ transition of aromatic sp2 domains. The other strong absorption peak at 340 nm is assigned to the n–π∗ transition of possible C=O or C=N groups present in N-CDs structure (Vercelli et al., 2021).

4. Scanning Electron Microscopy

The SEM of the CQDs was taken to determine the surface morphology and size distribution of the particles. It was seen that CQDs have spherical structures, and they were clustered with each other. Same morphology of CQDs was reported by (Lai et al., 2020).

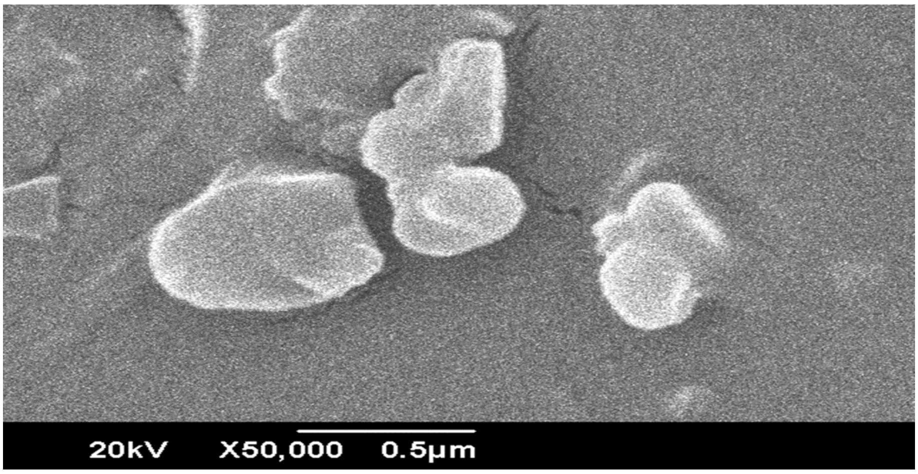

Figure 16: SEM image of CQDS - depicting the spherical and clustrous structure of CQDs

5. Energy Dispersive X-Ray Spectroscopy

The EDX of the CQDs was performed to determine elemental composition of the sample and following results were observed:

Table 2: EDX of CQDs - identifying the elemental composition of CQDs and weight percentage of each element.

ELEMENT	**WEIGHT%**	**MDL**	**ATOMIC %**	**ERROR %**
C	58.6	0.19	64.0	9.4
N	17.2	0.62	16.2	12.8
O	24.2	0.26	19.8	11.3

EDX analysis was performed to ensure the chemical composition carbon quantum dots (CQDs). The presence and percentages of carbon, nitrogen, and oxygen elements in the structure were also determined. Another study reported the same EDX analysis of CQDs.

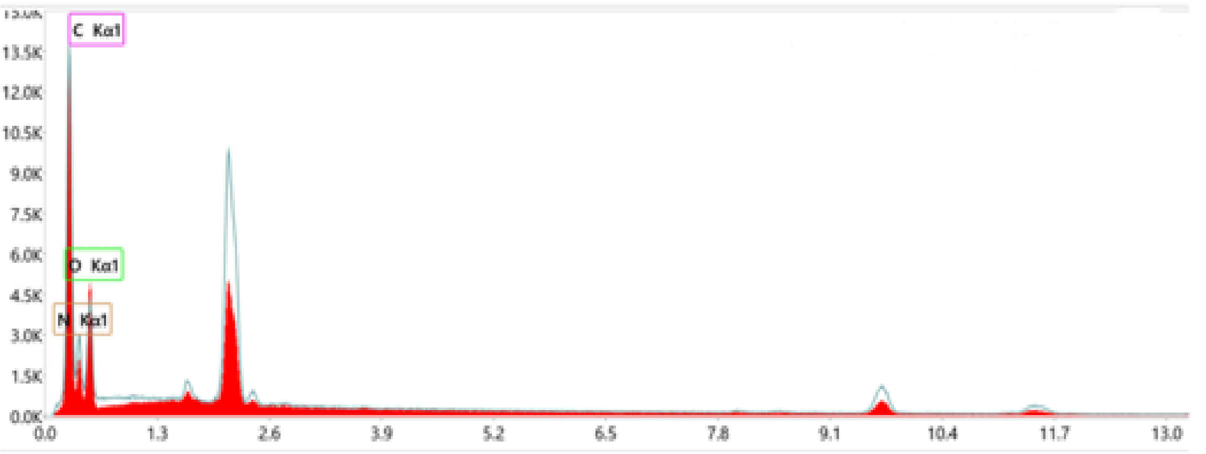

Figure 17: EDX spectrum of CQDs- indicating the respective peaks of each element identified in the EDX analysis.

6. Particle Size Analyzer

Analysis on particle size analyzer was also performed to confirm the size distribution range of CQDs. The range of the analyzer was 12nm onwards. No particle was detected by the machine, which confirmed that all the particles were less than 12nm.

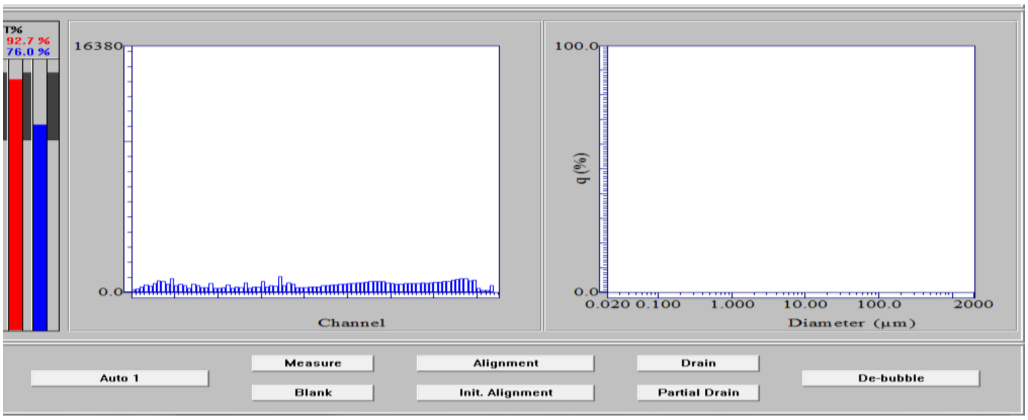

Figure 18: Particle size analyzer- CQDs were not detected by it confirming that its size was less than 10nm because the range of particle size analyzer was greater than 10nm.

4.1.3 Characterization of LCS:

Following analysis were performed to characterize LCS properly:

1. **Fourier-transform infrared spectroscopy**

The FTIR spectrum of the LCS sample was taken to study the chemical structure, type of bonds functional groups:

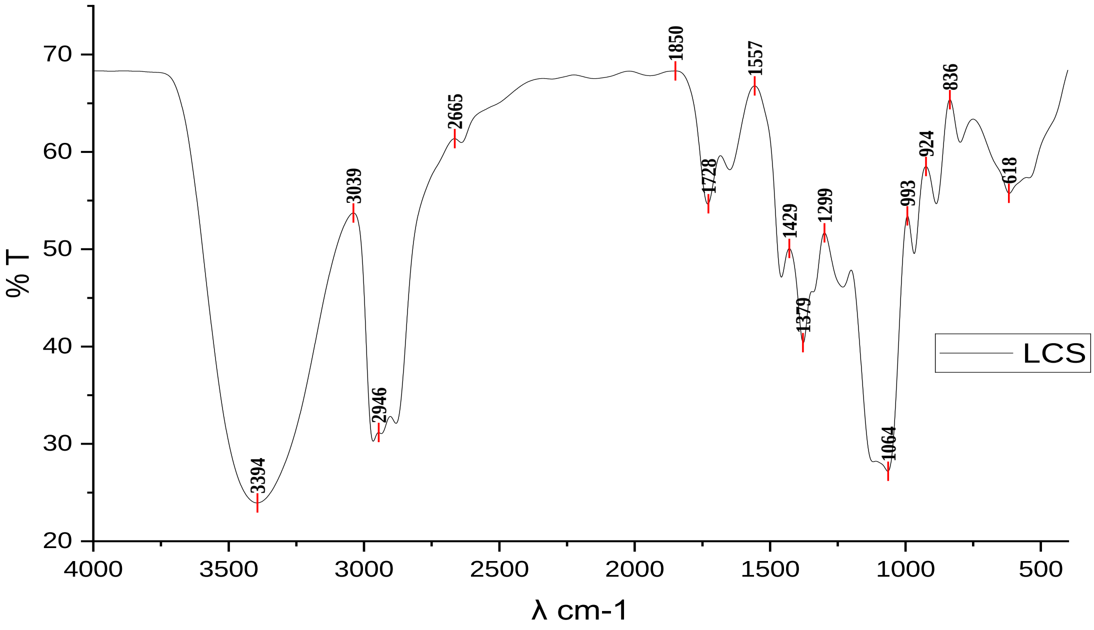

FIGURE 19: Fourier-transform infrared spectroscopy- FTIR spectrum of LCS identifying the key functional groups of LCS i.e OH, COOH bond and -COO- bond.

The LCS was obtained by liquifying the dried cotton straw powder by pyrolysis reaction with H_2SO_4, ethylene glycol and glycerol. FTIR spectrum of LCS represented two absorption peaks at 1649cm-1 and 1730cm-1 referring to the stretching vibration of -COOH bond and -COO- bond, identifying the breakdown of cellulose. The peak between 3395cm-1 and 2966cm-1 corresponds to the stretching vibrations of -OH bonds in the LCS that were established during the process of liquefaction. These characteristic peaks confirm the successful conversion of CS into LCS. Same types of peaks were reported by the study conducted by (Ma et al., 2018). Peaks at 1645cm-1 and 1724cm-1 were reported as the characteristic peaks of LCS.

2. Gas chromatography–mass spectrometry

Gas chromatography-mass spectrometry of LCS as reported by (Ma et al., 2018) was performed to identify the composition and percentage of poly-hydroxyl and hydroxyl compounds in it. For the formation of proper matrices of bio-polyurethane, when PAPI/MDI is added to LCS, major percentage of poly-hydroxyl compounds is required. The iso-cyanate group of PAPI/MDI reacts with poly-hydroxyl groups od LCS to form a thick and stable bio-polyurethane foam and its matrices. The following figure depicts the first 50 major peaks in the GC-MS chromatogram, according to which a major percentage of poly-hydroxyl compounds are present as compared to hydroxyl compounds:

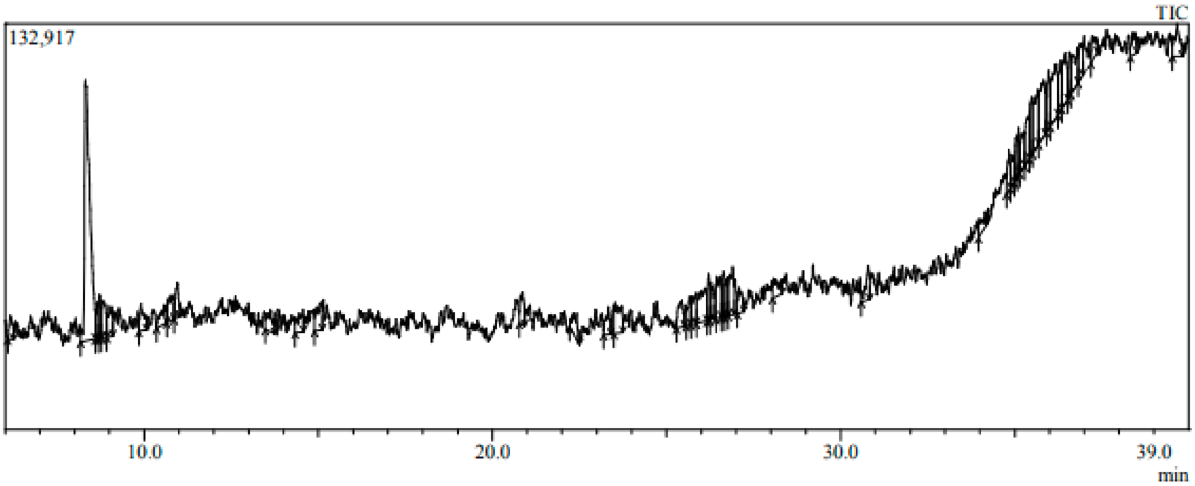

Figure 20: GC-MS chromatogram of LCS- first 50 peaks of compounds containing hydroxyl group.

The compounds present in these first 50 peaks are enlisted below and most of them are poly-hydroxyl compounds:

Table 3: Hydroxyl Compounds illustrated in GC-MS chromatogram of LCS as first 50 peaks.

Sr No.	Compound Name
1	Propanoic acid
2	2-[2-(Tert.butyl-dimethyl-siloxyl-methyl)
3	1,3-Dioxolane, 2,4,5-trimethyl
4	Acetonitrile, 2-[(1-ethyl-1H-1,2,3,4-tetrazol-5-y
5	Silane, trimethyl(methylenecyclopropyl)-
6	Butanetetrol
7	1,2-Dideoxy-l-erythro-pentitol
8	2-Hydroxy-2-methylbutyric acid
9	1,4,5-triol-3-one-1-carboxylic acid
10	1,3-Methylene-d-arabitol
11	Cyclohexanediol
12	2,3-Dibromo-1,4-butanediol
13	Protoadamanediol
14	Dibromophloretic acid
15	5-Methylthiazoline-2-resocinol
16	1,2-Dideoxy-l-erythro-pentitol
17	2-Propanol, 1,1'-oxybis
18	2-Hydroxyphenethyl alcohol
19	Hydrastininic acid
20	Hydroxybutyl methyl phenyl phosphine oxide
21	Chloroaniline-5-sulfonic acid
22	Butanoic acid
23	Carboxylic acid
24	Tartronic acid
25	Butoxycarbonyl 2-trifluoromethyl
26	Ethyl(hydroxymethyl)malonic acid
27	Cyclopentanetriol
28	1,6-Dideoxy-2,4-monoethylene-d-altritol
29	1,2-Dideoxy-l-erythro-pentitol
30	d-Altronic acid
31	1,3-Methylene-d-arabito
32	2-Hydroxy-2-methylbutyric acid
33	2-exo-5-endo-Protoadamanediol
34	5-tridecafluorohexyl
35	1,2-Propanediol
36	Uridine
37	1,3-Cyclohexanediol
38	Monomethylene-l-rhamnitol
39	Mucic acid
40	Dibromophloretic acid
41	Benzenedicarboxamide
42	Bis-dimethylaminomethyl-2,7-dihydroxy-fluorene
43	Imidazole-4,5-dicarboxamide
44	Ethanone

45	Hydrastininic acid
46	5-trans-Methyl-1R,3-cis-cyclohexanediol
47	isoindole-2-acetic acid
48	Benzenediol
49	Hydrocortisone
50	1,2-Propanediol,

According to GC-MS more than 200 of polyhroxyl compound and almost 100 hydroxyl compounds were identified, which confirms the successful formation of liquified cotton stalk from dried cotton stalk powder.

4.1.4 PHASE II- BPU COATED UREA

1. Scanning Electron Microscopy

SEM was used to check the coating structure and appearance of BPU coated urea (Ma et al., 2023):

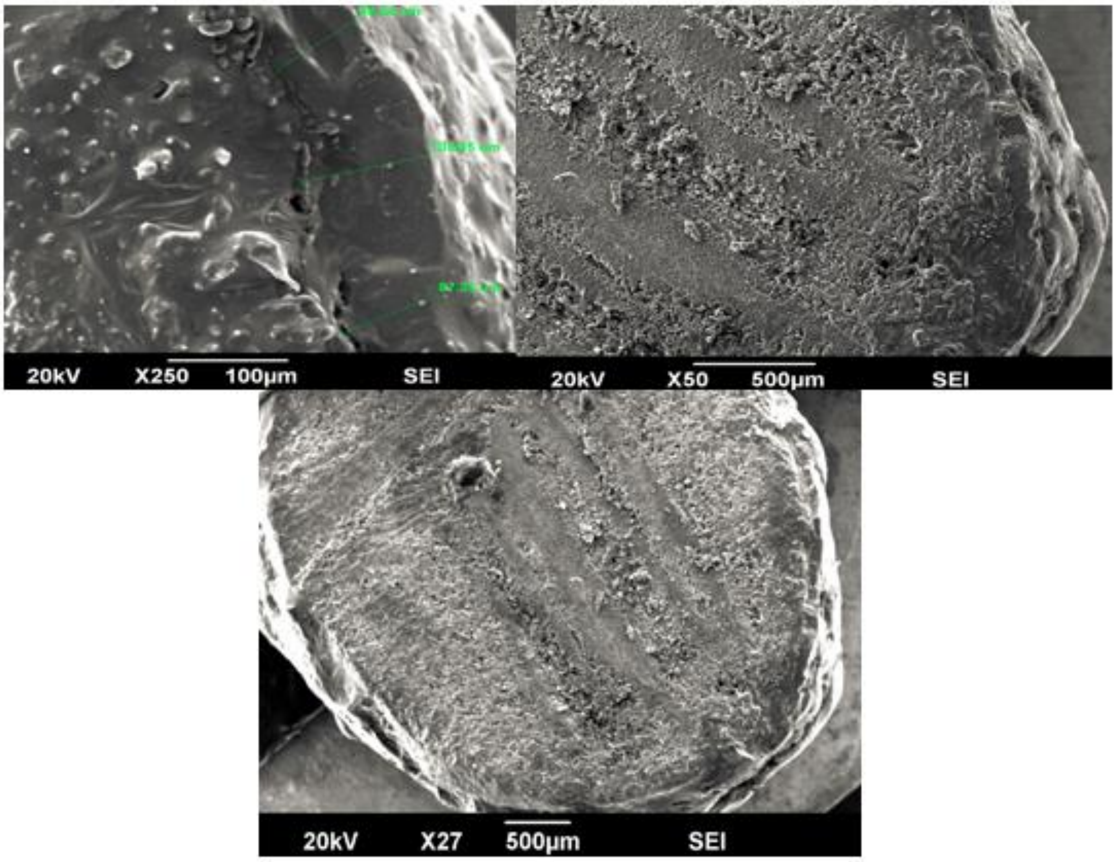

FIGURE 21: Scanning Electron microscopy- cross-sectional images of BPU coated urea- indicating the successful coating of bio-polyurethane on urea – coating thickness is also determined and labelled.

The internal portion of the above images is the Urea granule and the outer envelope like coating is BPU. The coating thickness ranges from 82µm to 110µm. It confirmed the successful formulation of BPU coating around the urea granule.

2. Fourier-transform infrared spectroscopy

FTIR was performed for both simple LCS and LCS with MDI (BPU). The following graph shows the spectrums of both:

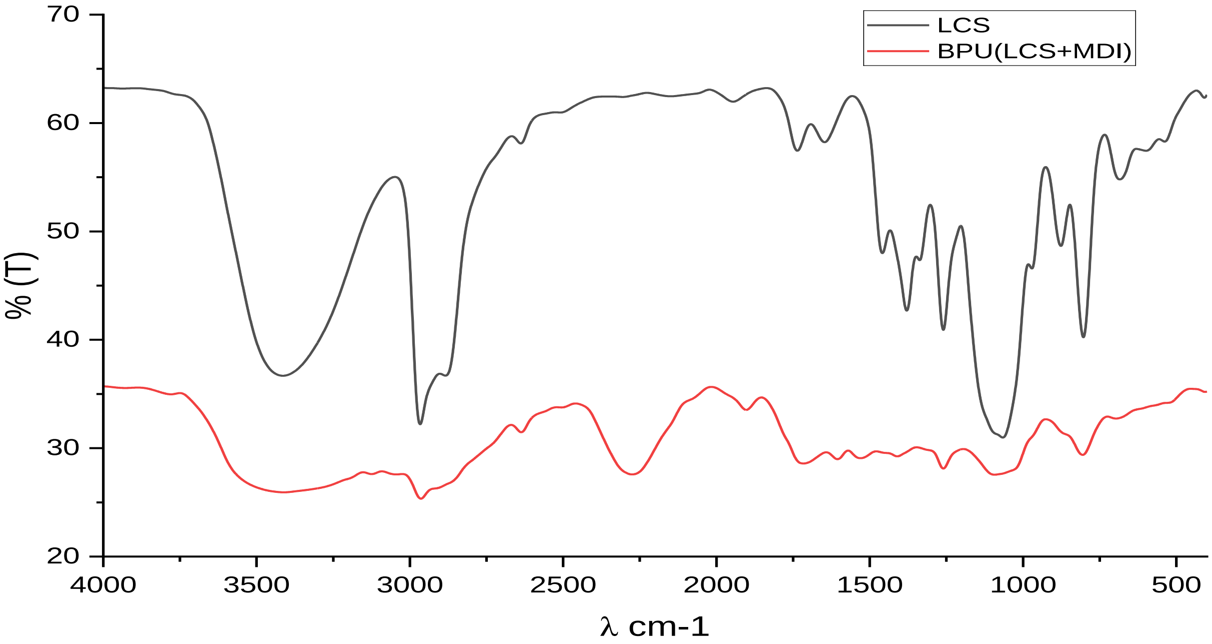

Figure 22: Fourier-transform infrared spectroscopy- FTIR spectrum comparison of LCS and BPU- depicting the disappearance of key functional group of LCS i.e. OH and appearance of NCO group, indicating the conversion of LCS into BPU.

For the LCS, two absorption peaks at 1645 cm−1 and 1724 cm−1 refers to the stretching vibration of -COOH and -COO- bond, denoting breakdown of the cellulose. The broad peak at 3500–3200 cm−1 symbolises the stretching vibrations of -OH bonds in the LCS and liquefaction phenomenon. It indicates that the CS-powder was converted into LCS successfully. For the BPU, the absorption peaks at 3311 cm−1, 1718 cm−1, 1597 cm−1, and 1217 cm−1 depicts the stretching vibration of N-H, C=O, βN-H, and C-O-C, respectively. After the polymerization reaction took place between LCS and PAPI, peaks of -OH between 3500–3200 cm−1 disappeared the characteristic absorption peaks of -NCO at 2270 cm−1 appears, confirming that the isocyanate groups reacted completely with the hydroxyl groups. Same phenomenon of peaks was reported by (Ma et al., 2018).

4.1.5 PHASE III

4.1.5.1 WATER RELEASE TESTS:

a) Cumulative N release rate:

The cumulative nitrogen release rate of dual coated urea in water at 25°C was assessed using Total Kjeldahl Nitrogen-TKN. The following graph depicts the N-release pattern of BPU coated urea and dual coated urea of both types i.e; ZnCQDs and CQDs+ZnO.

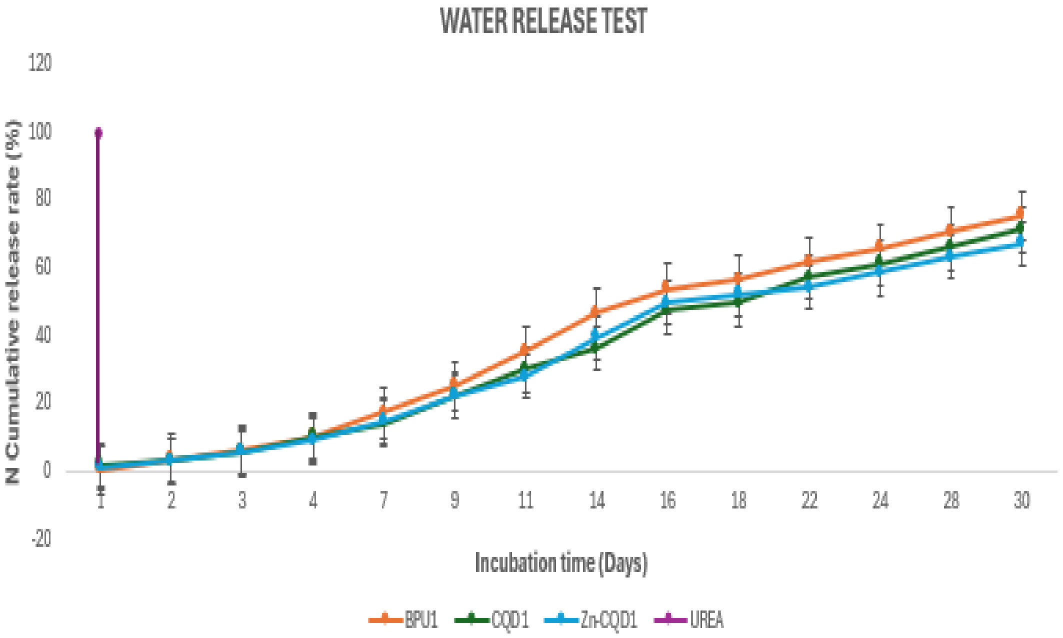

Figure 23: Water Release Test- cumulative nitrogen release percentage of urea, BPU and DCRFs- Urea was taken as control, DCRFs include the dual coated fertilizers with ZnCQDs and CQDs infused hydrogel.

The siloxane and polyether enhanced the hydrophobicity and grafted IPN structures in the coating. The IPN structure improved the behaviour of inactive components and improved the N release characteristics of all the coating combinations. As a result, the dual coated urea fertilizers met the standard of CRFs i,e; no more than 75% release in 28 days (ISO 18644:2016). The dual coated urea fertilizers, as compared to single coated BPU urea, performed a bit better. It can be concluded that hydrogel coating also improved the longevity of the cumulative N-release.

b) Cumulative Zn release rate:

Atomic Absorption Spectroscopy - AAS. The following graph depicts the Zn-release pattern dual coated urea fertilizer of both types i.e; ZnCQDs and CQDs+ZnO.

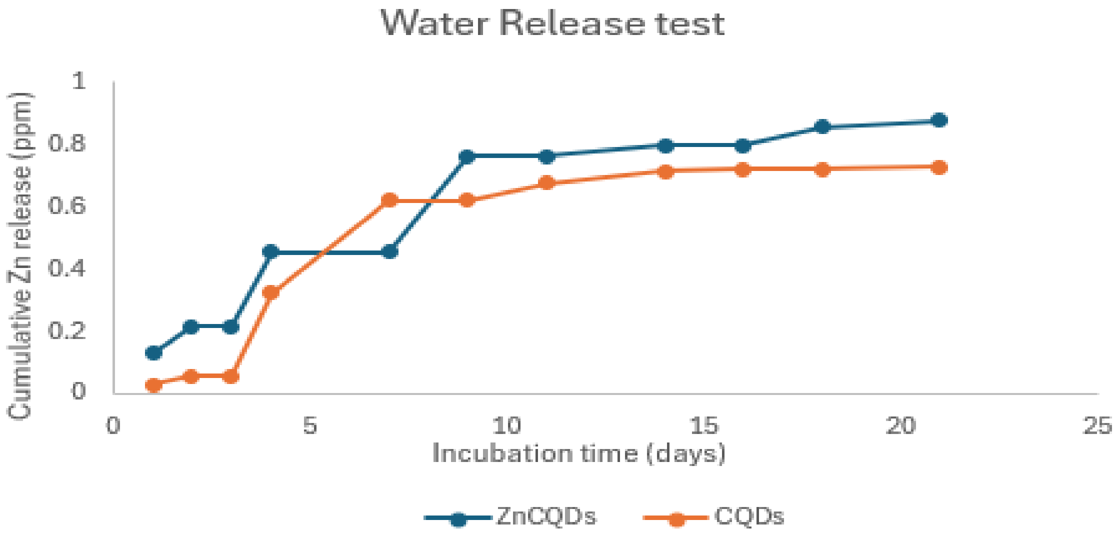

Figure 24: Water Release Test- cumulative zinc release percentage of DCRFs i.e. ZnCQDs and CQDs.

Zinc was infused in the outer hydrogel coating of DCRF in the form of ZnCQDs and CQDs+ZnO. Over the time period of 21 days, 0.9 ppm and 0.7 ppm of Zn was released by ZnCQDs and CQDs+ZnO, respectively. This concentration of Zn is optimum for the healthy growth of plants and grains.

3.1.2.4 SAND RELEASE TESTS:

a) Cumulative N release rate:

The cumulative nitrogen release rate of dual coated urea in sand at room temperature was assessed using Total Kjeldahl Nitrogen-TKN. The following graph depicts the N-release pattern of BPU coated urea and dual coated urea of both types i.e; ZnCQDs and CQDs+ZnO.

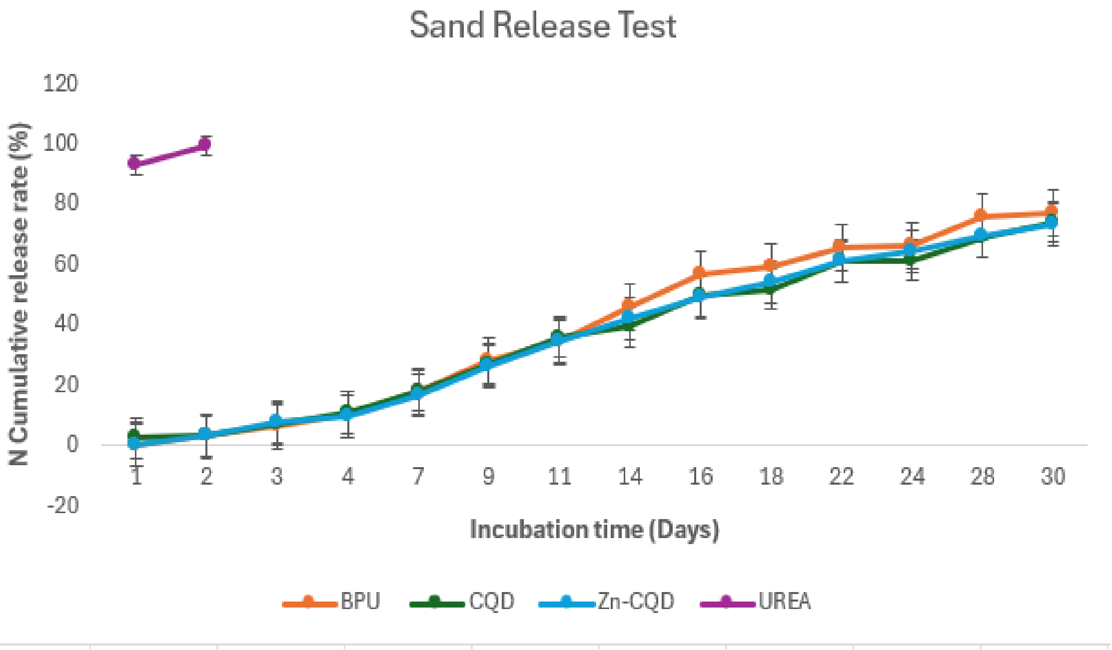

FIGURE 25: Sand Release Test- cumulative nitrogen release percentage of urea, BPU and DCRFs - Urea was taken as control, DCRFs include the dual coated fertilizers with ZnCQDs and CQDs infused hydrogel.

The siloxane and polyether enhanced the hydrophobicity and grafted IPN structures in the coating. The IPN structure improved the behaviour of inactive components and improved the N release characteristics of all the coating combinations. As a result, the dual coated urea fertilizers met the standard of CRFs i,e; no more than 75% release in 28 days (ISO 18644:2016). The dual coated urea fertilizers, as compared to single coated BPU urea, performed a bit better. It can be concluded that hydrogel coating also improved the longevity of the cumulative N-release.

b) Cumulative Zn release rate:

The cumulative Zn release rate of dual coated urea in sand at room temperature was assessed using Atomic Absorption Spectroscopy - AAS. The following graph depicts the Zn-release pattern dual coated urea fertilizer of both types i.e; ZnCQDs and CQDs+ZnO.

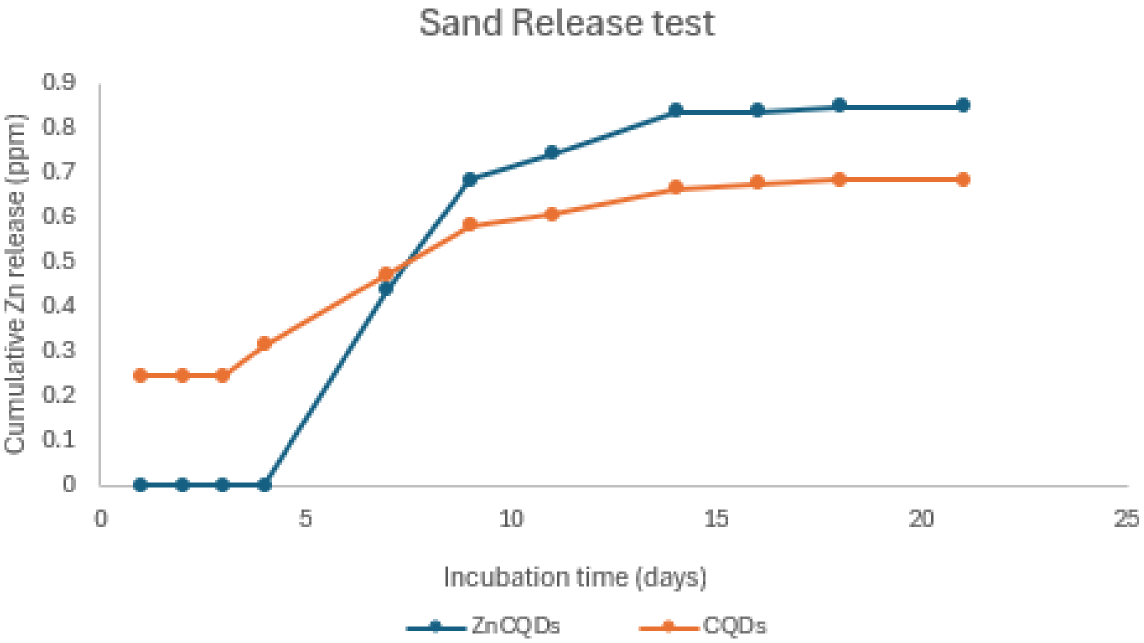

Figure 26: Sand Release Test- cumulative zinc release percentage of DCRFs i.e. ZnCQDs and CQDs.

Zinc was infused in the outer hydrogel coating of DCRF in the form of ZnCQDs and CQDs+ZnO. Over the time of 21 days, 1 ppm and 0.7 ppm of Zn concentrations were released by ZnCQDs and CQDs+ZnO, respectively. This concentration of Zn is optimum for the healthy growth of plants and grains.

4.1.5.3 Comparison of cumulative N% Release in water and sand:

The comparison of cumulative N% release by BPU-urea, ZnCQDs-DCRF and CQDs+ZnO-DCRF in water and sand was made to understand the behaviour of coating materials in different mediums. The following graph in figure 27 depicts this comparison. It was observed that the coating materials were almost unaffected by the change in medium. But it was also observed that both DCRFs performed a bit well than simple BPU-urea, by showing minor delay in release of N. It can be concluded that the formulated coatings can perform well in both mediums, and they are not affected much by the change in the environmental and physical factors. This aspect of coatings makes them unique from other types of coatings reported by the literature.

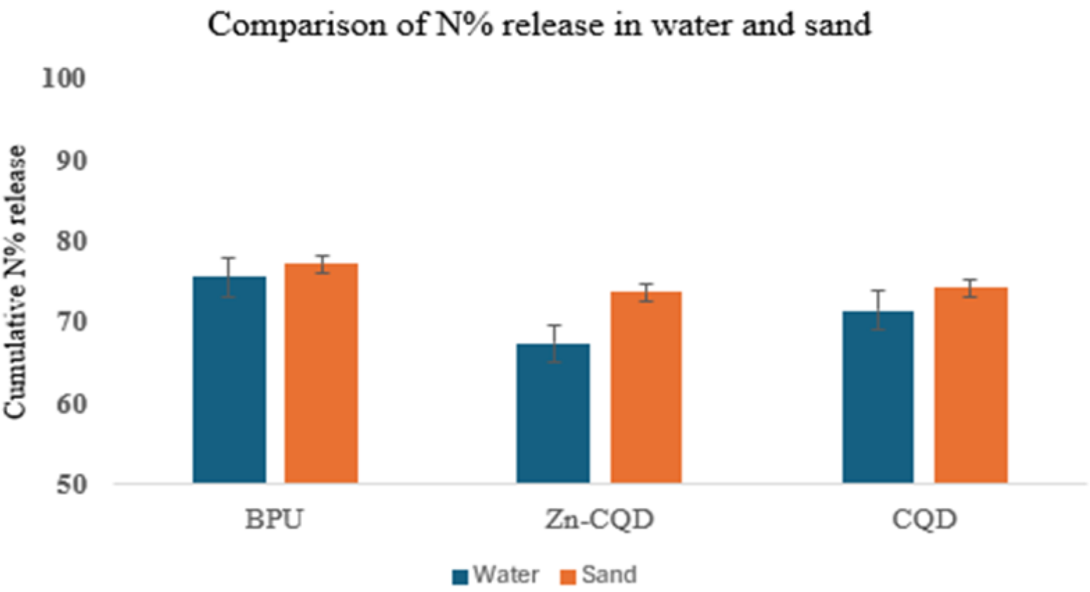

FIGURE 27: Comparison of cumulative nitrogen release percentage of BPU and DCRFs in water and sand.

4.1.5.4 Comparison of cumulative Zn Release by ZnCQDs-DCRF and CQDs+ZnO-DCRF:

To understand that which one of the ZnCQDs and CQDs+ZnO performed well in the release of Zn in both water and sand, a comparison was made, as shown in the following graph:

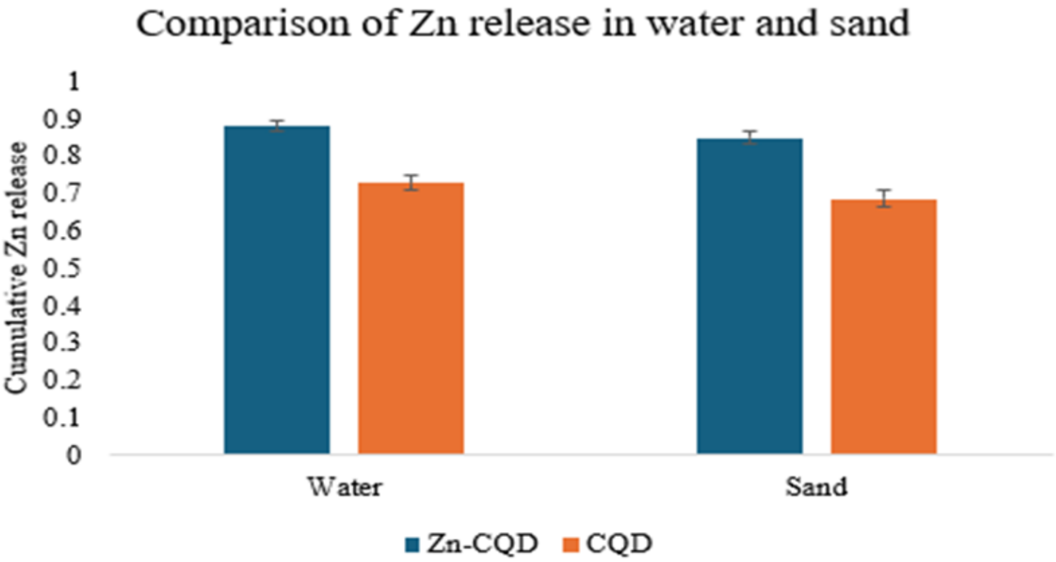

FIGURE 28: Comparison of cumulative zinc release percentage of DCRFs in water and sand.

ZnCQDs performed better than CQDs in the release of Zn in both sand and water. CQDs + ZnO also performed well in Zn release but the in ZnCQDs where zinc is doped and incorporated within their structure, it is released in a controlled manner with the required concentrations. It means we can control the concentration of Zn release by controlling the doping concentrations of Zn.

CHAPTER -V CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In this study, a dual coated control release urea fertilizer (DCRF) was developed using bio-based polymer and hydrogel infused with zinc doped carbon quantum dots and carbon quantum dots. This DCRF can slow-down and control the release concentration and patterns of nitrogen and zinc, or any other micronutrient added to it. The Nitrogen Release longevity of DCRF was up to the (ISO 18644:2016) standard for controlled release fertilizer, which states that a controlled release fertilizer should release no more than 75% of Nitrogen in water in 28 days. The DCRF also followed the standard sand column testing and in sand its Nitrogen Release longevity was 78% in 28 days. Zinc release of DCRF was up to 1ppm; requirement of Zn fertilizers, both in sand and water. Cumulative N and Zn release of DCRF was not affected much by the change in mediums, water and sand. Outer coating of hydrogel also increased the N-release longevity, apart from micronutrient supply. This double coating technique of fertilizer can be used with other microelements, as per the requirement of plants and crops. DCRF performs a lot better than traditional fertilizers such as chemical and petroleum-based fertilizers. It can also reduce the total fertilizer costs of any crop by saving Labor and time because it will be applied only once while conventional fertilizer needs to be applied twice or thrice per crop. This research fills in the gap of employing bio-synthesized polymers for the formulation and coating of controlled release fertilizers.

5.2 RECOMMENDATIONS

Following recommendations are made after the completion of the study:

- Estimate the release of zinc by controlling its doping concentration with CQDs. And understand their interaction of CQDs with fertilizers and crops
- Field-based testing should also be done to understand the real-world efficacy of DCRF.
- Laboratory scale pot experiments should be carried out on plants to understand the release patterns and behavior of DCRFS.
- Cost-Benefit analysis should be carried out in detail to evaluate the economic and financial status of the study.

CHAPTER -VI REFERENCES

6.1 REFERENCES

1. AbdElAziz, G. H., El-Rahman, A., Lamyaa, A., Ahmed, S. S., & Mahrous, S. E. M. (2021). Efficacy of ZnO nanoparticles as a remedial zinc fertilizer for soya bean and wheat corps. *Journal of Soil Sciences and Agricultural Engineering*, *12*(8), 573–582.
2. Abg Ahmad, D. F. B., Wasli, M. E., Tan, C. S. Y., Musa, Z., & Chin, S.-F. (2023). Eco-friendly cellulose hydrogels as controlled release fertilizer for enhanced growth and yield of upland rice. *Scientific Reports*, *13*(1), 20453.
3. Ahsan, A. K., Tebha, S. S., Sangi, R., Kamran, A., Zaidi, Z. A., Haque, T., & Ali Hamza, M. S. (2021). Zinc micronutrient deficiency and its prevalence in malnourished pediatric children as compared to well-nourished children: a nutritional emergency. *Global Pediatric Health*, *8*, 2333794X211050316.
4. Alexandratos, N., & Bruinsma, J. (2012). *World agriculture towards 2030/2050: the 2012 revision*.
5. Alikhani, M., Mirbolook, A., Sadeghi, J., & Lakzian, A. (2023a). Effect of a new slow-release zinc fertilizer based on carbon dots on the zinc concentration, growth indices, and yield in wheat (Triticum aestivum). *Plant Physiology and Biochemistry*, *200*, 107783.
6. Alikhani, M., Mirbolook, A., Sadeghi, J., & Lakzian, A. (2023b). Improving Wheat Growth and Nutrient Uptake in Calcareous Soil: a Novel Approach with Carbon Dots as a Slow-Release Zinc Fertilizer. *Journal of Soil Science and Plant Nutrition*, *23*(4), 6232–6245.
7. Annapurna, S. M., Niketh, S., Ashok, D., & Madhu, G. M. (2020). Review on sustained fertilizers releases for agriculture systems. *Int J Adv Res Eng Technol*, *11*(12), 2827–2835.
8. Aslan, M., & Eskalen, H. (2021). A study of carbon nanodots (carbon quantum dots) synthesized from tangerine juice using one-step hydrothermal method. *Fullerenes, Nanotubes and Carbon Nanostructures*, *29*(12), 1026–1033.

9. Atchudan, R., Edison, T. N. J. I., Mani, S., Perumal, S., Vinodh, R., Thirunavukkarasu, S., & Lee, Y. R. (2020). Facile synthesis of a novel nitrogen-doped carbon dot adorned zinc oxide composite for photodegradation of methylene blue. *Dalton Transactions*, *49*(48), 17725–17736.
10. Ayiti, O. E., & Babalola, O. O. (2022). Factors influencing soil nitrification process and the effect on environment and health. *Frontiers in Sustainable Food Systems*, *6*, 821994.
11. Basta, A. H., Lotfy, V. F., & Eldewany, C. (2021). Comparison of copper-crosslinked carboxymethyl cellulose versus biopolymer-based hydrogels for controlled release of fertilizer. *Polymer-Plastics Technology and Materials*, *60*(17), 1884–1897.
12. Beig, B., Niazi, M. B. K., Jahan, Z., Haider, G., Zia, M., Shah, G. A., Iqbal, Z., & Hayat, A. (2023). Development and testing of zinc sulfate and zinc oxide nanoparticle-coated urea fertilizer to improve N and Zn use efficiency. *Frontiers in Plant Science*, *13*, 1058219.
13. Beig, B., Niazi, M. B. K., Ullah, B., Gondal, A. N., Jahan, Z., Zia, M., & Ahmad, N. (2024). Effect of zinc oxide and zinc oxide nanoparticles coating on urea diffusion and its release kinetics for design and development of slow-release fertilizer: an experimental and numerical investigation. *Journal of Coatings Technology and Research*, *21*(1), 199–213.
14. Cao, M. L., Li, Y. X., & Du, H. L. (2020). Effects of exogenous zinc on the photosynthesis and carbonic anhydrase activity of millet (Setaria italica L.). *Photosynthetica*, *58*(3).
15. Channab, B.-E., El Idrissi, A., Zahouily, M., Essamlali, Y., & White, J. C. (2023). Starch-based controlled release fertilizers: a review. *International Journal of Biological Macromolecules*, *238*, 124075.
16. Chao-Mujica, F. J., Garcia-Hernández, L., Camacho-López, S., Camacho-López, M., Camacho-López, M. A., Reyes Contreras, D., Pérez-Rodríguez, A., Peña-Caravaca, J. P., Páez-Rodríguez, A., & Darias-Gonzalez, J. G. (2021). Carbon quantum dots by submerged arc discharge in water: Synthesis, characterization, and mechanism of formation. *Journal of Applied Physics*, *129*(16).

17. Chasapis, C. T., Ntoupa, P.-S. A., Spiliopoulou, C. A., & Stefanidou, M. E. (2020). Recent aspects of the effects of zinc on human health. *Archives of Toxicology*, *94*, 1443–1460.
18. Chaudhary, V., & Yeshpal, N. (2023). Bio-polymer based slow release/control release fertilizer. *Res. Jr. Agril. Sci*, *14*(5), 1234–1240.
19. Chen, Y., Mi, H., Zhang, Y., Zhang, G., Li, C., Ye, Y., Zhang, R., Shi, J., Li, Z., & Tian, X. (2022). Impact of ZnSO4 and ZnEDTA applications on wheat Zn biofortification, soil Zn fractions and bacterial community: Significance for public health and agroecological environment. *Applied Soil Ecology*, *176*, 104484.
20. Choudhary, M., Muduli, M., & Ray, S. (2022). A comprehensive review on nitrate pollution and its remediation: Conventional and recent approaches. *Sustainable Water Resources Management*, *8*(4), 113.
21. Cuajungco, M. P., Ramirez, M. S., & Tolmasky, M. E. (2021). Zinc: Multidimensional effects on living organisms. *Biomedicines*, *9*(2), 208.
22. Cui, L., Ren, X., Wang, J., & Sun, M. (2020). Synthesis of homogeneous carbon quantum dots by ultrafast dual-beam pulsed laser ablation for bioimaging. *Materials Today Nano*, *12*, 100091.
23. Dai, Z., Yu, M., Chen, H., Zhao, H., Huang, Y., Su, W., Xia, F., Chang, S. X., Brookes, P. C., & Dahlgren, R. A. (2020). Elevated temperature shifts soil N cycling from microbial immobilization to enhanced mineralization, nitrification and denitrification across global terrestrial ecosystems. *Global Change Biology*, *26*(9), 5267–5276.
24. Davies, B., Coulter, J. A., & Pagliari, P. H. (2022). Soil enzyme activity behavior after urea nitrogen application. *Plants*, *11*(17), 2247.
25. de Francisco, M., Romeiro, A., Durães, L., Álvarez-Torrellas, S., Ibañez, M. A., & Almendros, P. (2024). Environmental Behaviour of Synthesized and Commercial Agricultural Zinc Products: Leaching, Migration, and Availability in Soils. *Journal of Soil Science and Plant Nutrition*, 1–16.
26. Dembedza, M. P., Chopera, P., & Matsungo, T. M. (2024). Risk of zinc deficiency among children aged 0–59 months in sub-Saharan Africa: a narrative review. *South African Journal of Clinical Nutrition*, *37*(2), 69–76.

27. Dhaliwal, S. S., Sharma, V., Shukla, A. K., Kaur, J., Verma, V., Kaur, M., Singh, P., Gaber, A., & Hossain, A. (2022). Zinc-Based Mineral (ZnSO4·7H2O) and Chelated (Zn-EDTA) Fertilizers improve the Productivity, Quality and Efficiency Indices of Field Pea (Pisum sativum L.) through Biofortification. *Journal of Trace Elements and Minerals*, *2*, 100033.
28. Dsouza, S. D., Buerkle, M., Brunet, P., Maddi, C., Padmanaban, D. B., Morelli, A., Payam, A. F., Maguire, P., Mariotti, D., & Svrcek, V. (2021). The importance of surface states in N-doped carbon quantum dots. *Carbon*, *183*, 1–11.
29. Dubey, P. K., Singh, G. S., Abhilash, P. C., Dubey, P. K., Singh, G. S., & Abhilash, P. C. (2020). Agriculture in a changing climate. *Adaptive Agricultural Practices: Building Resilience in a Changing Climate*, 1–10.
30. El-Ghamry, A., El-Naggar, E.-S., Elgorban, A. M., Gao, B., Ahmad, Z., & Mosa, A. (2021). Double Coating as a Novel Technology for Controlling Urea Dissolution in Soil: A Step toward Improving the Sustainability of Nitrogen Fertilization Approaches. *Sustainability*, *13*(19), 10707.
31. Eskalen, H. (2020). Influence of carbon quantum dots on electro–optical performance of nematic liquid crystal. *Applied Physics A*, *126*(9), 708.
32. Fachini, J., de Figueiredo, C. C., & do Vale, A. T. (2022). Assessing potassium release in natural silica sand from novel K-enriched sewage sludge biochar fertilizers. *Journal of Environmental Management*, *314*, 115080.
33. Fertahi, S., Ilsouk, M., Zeroual, Y., Oukarroum, A., & Barakat, A. (2021). Recent trends in organic coating based on biopolymers and biomass for controlled and slow release fertilizers. *Journal of Controlled Release*, *330*, 341–361.
34. Firmanda, A., Fahma, F., Syamsu, K., Suryanegara, L., & Wood, K. (2022). Controlled/slow-release fertilizer based on cellulose composite and its impact on sustainable agriculture. *Biofuels, Bioproducts and Biorefining*, *16*(6), 1909–1930.
35. Freitas, T., Oliveira, D. P., Dutra, M. P., Zito, P. C., Reis, E. A. C., Fernandes, T. J., Nunes, A. P. P., Guimarães, R. J., Rabêlo, F. H. S., & Guelfi, D. (2023). Blending Controlled-Release and Urease-Inhibitor

Technologies as Innovative Solutions to Reduce Ammonia Emissions in Coffee Environments. *Soil Systems*, *7*(4), 83.

36. Gao, W., Fan, C., Zhang, W., Li, N., Liu, H., & Chen, M. (2023). Heterotrophic nitrification of organic nitrogen in soils: process, regulation, and ecological significance. *Biology and Fertility of Soils*, *59*(3), 261–274.
37. Ghumman, A. S. M., Shamsuddin, R., Nasef, M. M., Yahya, W. Z. N., Abbasi, A., & Almohamadi, H. (2022). Sulfur enriched slow-release coated urea produced from inverse vulcanized copolymer. *Science of The Total Environment*, *846*, 157417.
38. Goyal, A., & Qanungo, K. (2023). Nitrous oxide as a greenhouse gas: A state of art. *AIP Conference Proceedings*, *2535*(1).
39. Gu, D., Andreev, K., & Dupre, M. E. (2021). Major trends in population growth around the world. *China CDC Weekly*, *3*(28), 604.
40. Gupta, S., Brazier, A. K. M., & Lowe, N. M. (2020). Zinc deficiency in low-and middle-income countries: prevalence and approaches for mitigation. *Journal of Human Nutrition and Dietetics*, *33*(5), 624–643.
41. Hacisalihoglu, G. (2020). Zinc (Zn): The last nutrient in the alphabet and shedding light on Zn efficiency for the future of crop production under suboptimal Zn. *Plants*, *9*(11), 1471.
42. Hagiwara, K., Horikoshi, S., & Serpone, N. (2021). Photoluminescent carbon quantum dots: synthetic approaches and photophysical properties. *Chemistry–A European Journal*, *27*(37), 9466–9481.
43. Hamzah Saleem, M., Usman, K., Rizwan, M., Al Jabri, H., & Alsafran, M. (2022). Functions and strategies for enhancing zinc availability in plants for sustainable agriculture. *Frontiers in Plant Science*, *13*, 1033092.
44. Han, G., Qiao, Z., Li, Y., Wang, C., & Wang, B. (2021). The roles of CCCH zinc-finger proteins in plant abiotic stress tolerance. *International Journal of Molecular Sciences*, *22*(15), 8327.
45. He, H., Yang, Y., Li, J., Lai, X., Chen, X., Wang, L., Zhang, W., Huang, Y., & Zhang, P. (2021). Enhanced fluorescence of Zn-doped carbon quantum dots using zinc citrate chelate as precursor for fluorescent sensor applications. *Materials Science and Engineering: B*, *264*, 114955.

46. Hesari, M., & Ding, Z. (2020). A perspective on application of carbon quantum dots in luminescence immunoassays. *Frontiers in Chemistry*, *8*, 580033.

47. Highton, M. P., Bakken, L. R., Dörsch, P., Molstad, L., & Morales, S. E. (2022). Nitrite accumulation and impairment of N2O reduction explains contrasting soil denitrification phenotypes. *Soil Biology and Biochemistry*, *166*, 108529.

48. Hussein, S. A., Lateef, M. A., & Al-Qady, R. A. (2021). The Effect of Foliar Application of Iron, Chelated Zink, And Gibberellin on Some of the Vegetative Growth Parameters of Olive Seedlings Cultivar (Sorani). *International Journal of Agricultural and Statistical Sciences*, *3899*, 17–1497.

49. Jariwala, H., Santos, R. M., Lauzon, J. D., Dutta, A., & Wai Chiang, Y. (2022). Controlled release fertilizers (CRFs) for climate-smart agriculture practices: a comprehensive review on release mechanism, materials, methods of preparation, and effect on environmental parameters. *Environmental Science and Pollution Research*, *29*(36), 53967–53995.

50. Jha, S., & Yadav, A. (2023). Assessment of carbon and fullerene nanomaterials for sustainable crop plants growth and production. In *Engineered Nanomaterials for Sustainable Agricultural Production, Soil Improvement and Stress Management* (pp. 145–160). Elsevier.

51. Jia, J., Sun, Y., Zhang, Y., Liu, Q., Cao, J., Huang, G., Xing, B., Zhang, C., Zhang, L., & Cao, Y. (2020). Facile and efficient fabrication of bandgap tunable carbon quantum dots derived from anthracite and their photoluminescence properties. *Frontiers in Chemistry*, *8*, 123.

52. John, V. L., Nair, Y., & Vinod, T. P. (2021). Doping and surface modification of carbon quantum dots for enhanced functionalities and related applications. *Particle & Particle Systems Characterization*, *38*(11), 2100170.

53. Jun, W., Zhang, Z., Liang, F., Zhao, C. H. E., Yongkang, W. E. N., Zhang, M., Wenjun, J. I. N., Zhaorong, D., & He, S. (2024). Decreased soil pH weakens the positive rhizosphere effect on denitrification capacity. *Pedosphere*, *34*(5), 905–915.

54. Khan, M. E., Mohammad, A., & Yoon, T. (2022). State-of-the-art developments in carbon quantum dots (CQDs): Photo-catalysis, bio-imaging, and bio-sensing applications. *Chemosphere*, *302*, 134815.
55. Khan, S. T., Malik, A., Alwarthan, A., & Shaik, M. R. (2022). The enormity of the zinc deficiency problem and available solutions; an overview. *Arabian Journal of Chemistry*, *15*(3), 103668.
56. Klimczyk, M., Siczek, A., & Schimmelpfennig, L. (2021). Improving the efficiency of urea-based fertilization leading to reduction in ammonia emission. *Science of the Total Environment*, *771*, 145483.
57. Kou, X., Jiang, S., Park, S.-J., & Meng, L.-Y. (2020). A review: recent advances in preparations and applications of heteroatom-doped carbon quantum dots. *Dalton Transactions*, *49*(21), 6915–6938.
58. Kurniawati, P., Purbaningtias, T. E., Wiyantoko, B., & Dewi, G. (2021). Analytical method validation for cobalt determination on organic fertilizer. *AIP Conference Proceedings*, *2370*(1).
59. Lai, X., Liu, C., He, H., Li, J., Wang, L., Long, Q., Zhang, P., & Huang, Y. (2020a). Hydrothermal synthesis and characterization of nitrogen-doped fluorescent carbon quantum dots from citric acid and urea. *Ferroelectrics*, *566*(1), 116–123.
60. Lai, X., Liu, C., He, H., Li, J., Wang, L., Long, Q., Zhang, P., & Huang, Y. (2020b). Hydrothermal synthesis and characterization of nitrogen-doped fluorescent carbon quantum dots from citric acid and urea. *Ferroelectrics*, *566*(1), 116–123.
61. Lakshmi, P. V., Singh, S. K., Pramanick, B., Kumar, M., Laik, R., Kumari, A., Shukla, A. K., Abdel Latef, A. A. H., Ali, O. M., & Hossain, A. (2021). Long-term zinc fertilization in calcareous soils improves wheat (Triticum aestivum L.) productivity and soil zinc status in the rice–wheat cropping system. *Agronomy*, *11*(7), 1306.
62. Li, T., Wang, Z., Wang, C., Huang, J., Feng, Y., Shen, W., Zhou, M., & Yang, L. (2022). Ammonia volatilization mitigation in crop farming: A review of fertilizer amendment technologies and mechanisms. *Chemosphere*, *303*, 134944.

63. LI, Y., LI, R., ZHANG, Y., WANG, R., & LIU, Y. (2024). Zinc deficiency during pregnancy and its effect on pregnancy outcome. *Basic & Clinical Medicine*, *44*(4), 422.
64. Li, Z., Tang, Z., Song, Z., Chen, W., Tian, D., Tang, S., Wang, X., Wang, J., Liu, W., & Wang, Y. (2022). Variations and controlling factors of soil denitrification rate. *Global Change Biology*, *28*(6), 2133–2145.
65. Li, Z., & Zhang, M. (2023). Progress in the preparation of stimulus-responsive cellulose hydrogels and their application in slow-release fertilizers. *Polymers*, *15*(17), 3643.
66. Liao, F., Lilay, G. H., Castro, P. H., Azevedo, H., & Assunção, A. G. L. (2022). Regulation of the zinc deficiency response in the legume model Medicago truncatula. *Frontiers in Plant Science*, *13*, 916168.
67. Liao, J., Luo, Q., Hu, A., Wan, W., Tian, D., Ma, J., Ma, T., Luo, H., & Lu, S. (2022). Soil moisture–atmosphere feedback dominates land N2O nitrification emissions and denitrification reduction. *Global Change Biology*, *28*(21), 6404–6418.
68. Lin, J., Bjørk, P. K., Kolte, M. V, Poulsen, E., Dedic, E., Drace, T., Andersen, S. U., Nadzieja, M., Liu, H., & Castillo-Michel, H. (2024). Zinc mediates control of nitrogen fixation via transcription factor filamentation. *Nature*, *631*(8019), 164–169.
69. Lin, W., Luo, H., Wu, J., Hung, T.-C., Cao, B., Liu, X., Yang, J., & Yang, P. (2022). A review of the emerging risks of acute ammonia nitrogen toxicity to aquatic decapod crustaceans. *Water*, *15*(1), 27.
70. Luo, W., Wang, Y., Lin, F., Liu, Y., Gu, R., Liu, W., & Xiao, C. (2020). Selenium-doped carbon quantum dots efficiently ameliorate secondary spinal cord injury via scavenging reactive oxygen species. *International Journal of Nanomedicine*, 10113–10125.
71. Ma, X., Chen, J., Yang, Y., Su, X., Zhang, S., Gao, B., & Li, Y. C. (2018). Siloxane and polyether dual modification improves hydrophobicity and interpenetrating polymer network of bio-polymer for coated fertilizers with enhanced slow release characteristics. *Chemical Engineering Journal*, *350*, 1125–1134.
72. Ma, X., Zhang, S., Yang, Y., Tong, Z., Shen, T., Yu, Z., Xie, J., Yao, Y., Gao, B., & Li, Y. C. (2023). Development of multifunctional copper

alginate and bio-polyurethane bilayer coated fertilizer: Controlled-release, selenium supply and antifungal. *International Journal of Biological Macromolecules*, *224*, 256–265.

73. Madan, B., Malik, A., & Raghuram, N. (2022). Crop nitrogen use efficiency for sustainable food security and climate change mitigation. *Plant Nutrition and Food Security in the Era of Climate Change*, 47–72.
74. Manikandan, V., & Lee, N. Y. (2022). Green synthesis of carbon quantum dots and their environmental applications. *Environmental Research*, *212*, 113283.
75. Mansouri, H., Ait Said, H., Noukrati, H., Oukarroum, A., Ben youcef, H., & Perreault, F. (2023). Advances in Controlled Release Fertilizers: Cost-Effective Coating Techniques and Smart Stimuli-Responsive Hydrogels. *Advanced Sustainable Systems*, *7*(9), 2300149.
76. Martin, K. R., & Bloomer, R. J. (2022). Nitrate and human health: An overview. *Nitrate Handbook*, 303–345.
77. Martínez-Dalmau, J., Berbel, J., & Ordóñez-Fernández, R. (2021). Nitrogen fertilization. A review of the risks associated with the inefficiency of its use and policy responses. *Sustainability*, *13*(10), 5625.
78. Meraz-Dávila, S., Pérez-García, C. E., & Feregrino-Perez, A. A. (2021). Challenges and advantages of electrospun nanofibers in agriculture: a review. *Materials Research Express*, *8*(4), 042001.
79. Mirbolook, A., Sadaghiani, M. R., Keshavarz, P., & Alikhani, M. (2023). New slow-release urea fertilizer fortified with zinc for improving zinc availability and nitrogen use efficiency in maize. *ACS Omega*, *8*(48), 45715–45728.
80. Molaei, M. J. (2020). Principles, mechanisms, and application of carbon quantum dots in sensors: a review. *Analytical Methods*, *12*(10), 1266–1287.
81. Montalvo, D., Degryse, F., Da Silva, R. C., Baird, R., & McLaughlin, M. J. (2016). Agronomic effectiveness of zinc sources as micronutrient fertilizer. *Advances in Agronomy*, *139*, 215–267.
82. Moradi, S., Babapoor, A., Ghanbarlou, S., Kalashgarani, M. Y., Salahshoori, I., & Seyfaee, A. (2024). Toward a new generation of

fertilizers with the approach of controlled-release fertilizers: a review. *Journal of Coatings Technology and Research*, *21*(1), 31–54.

83. Motasim, A. M., Samsuri, A. W., Nabayi, A., Akter, A., Haque, M. A., Abdul Sukor, A. S., & Adibah, A. M. (2024a). Urea application in soil: Processes, losses, and alternatives—A review. *Discover Agriculture*, *2*(1), 42.
84. Motasim, A. M., Samsuri, A. W., Nabayi, A., Akter, A., Haque, M. A., Abdul Sukor, A. S., & Adibah, A. M. (2024b). Urea application in soil: Processes, losses, and alternatives—A review. *Discover Agriculture*, *2*(1), 42.
85. Mousavi, S. M., Sedaghat, A., & Esmaeili, M. (2024). Zinc in plants: biochemical functions and dependent signaling. In *Metals and Metalloids in Plant Signaling* (pp. 241–263). Springer.
86. Nasiadek, M., Stragierowicz, J., Klimczak, M., & Kilanowicz, A. (2020). The role of zinc in selected female reproductive system disorders. *Nutrients*, *12*(8), 2464.
87. Natasha, N., Shahid, M., Bibi, I., Iqbal, J., Khalid, S., Murtaza, B., Bakhat, H. F., Farooq, A. B. U., Amjad, M., & Hammad, H. M. (2022). Zinc in soil-plant-human system: A data-analysis review. *Science of the Total Environment*, *808*, 152024.
88. Ni, K., & Pacholski, A. S. (2022). Soil Moisture and Temperature Effects on Granule Dissolution and Urease Activity of Urea with and without Inhibitors—An Incubation Study. *Agriculture*, *12*(12), 2037.
89. Oh, S., Cho, K., Park, S., Kwon, M. J., Chung, J., & Lee, S. (2023). Denitrification dynamics in unsaturated soils with different porous structures and water saturation degrees: A focus on the shift in microbial community structures. *Journal of Hazardous Materials*, *445*, 130413.
90. Pahalvi, H. N., Rafiya, L., Rashid, S., Nisar, B., & Kamili, A. N. (2021). Chemical fertilizers and their impact on soil health. *Microbiota and Biofertilizers, Vol 2: Ecofriendly Tools for Reclamation of Degraded Soil Environs*, 1–20.
91. Palacio-Vergara, M., Álvarez-Gómez, M., Gallego, J., & López, D. (2023). Biomass solvothermal treatment methodologies to obtain carbon quantum dots: A systematic review. *Talanta Open*, 100244.

92. Pandiyan, S., Arumugam, L., Srirengan, S. P., Pitchan, R., Sevugan, P., Kannan, K., Pitchan, G., Hegde, T. A., & Gandhirajan, V. (2020). Biocompatible carbon quantum dots derived from sugarcane industrial wastes for effective nonlinear optical behavior and antimicrobial activity applications. *ACS Omega*, *5*(47), 30363–30372.
93. Patel, D. K., Kim, H.-B., Dutta, S. D., Ganguly, K., & Lim, K.-T. (2020). Carbon nanotubes-based nanomaterials and their agricultural and biotechnological applications. *Materials*, *13*(7), 1679.
94. Praharaj, S., Skalicky, M., Maitra, S., Bhadra, P., Shankar, T., Brestic, M., Hejnak, V., Vachova, P., & Hossain, A. (2021). Zinc biofortification in food crops could alleviate the zinc malnutrition in human health. *Molecules*, *26*(12), 3509.
95. Pramanik, P., Krishnan, P., Maity, A., Mridha, N., Mukherjee, A., & Rai, V. (2020). Application of nanotechnology in agriculture. *Environmental Nanotechnology Volume 4*, 317–348.
96. Rahman, M. H., Haque, K. M. S., & Khan, M. Z. H. (2021). A review on application of controlled released fertilizers influencing the sustainable agricultural production: A Cleaner production process. *Environmental Technology & Innovation*, *23*, 101697.
97. Rai-Kalal, P., & Jajoo, A. (2021). Priming with zinc oxide nanoparticles improve germination and photosynthetic performance in wheat. *Plant Physiology and Biochemistry*, *160*, 341–351.
98. Ramzan, S., Rasool, T., Bhat, R. A., Ahmad, P., Ashraf, I., Rashid, N., ul Shafiq, M., & Mir, I. A. (2020). Agricultural soils a trigger to nitrous oxide: A persuasive greenhouse gas and its management. *Environmental Monitoring and Assessment*, *192*, 1–21.
99. Ramzan, Y., Hafeez, M. B., Khan, S., Nadeem, M., Batool, S., & Ahmad, J. (2020). Biofortification with zinc and iron improves the grain quality and yield of wheat crop. *International Journal of Plant Production*, *14*(3), 501–510.
100. Ransom, C. J., Jolley, V. D., Blair, T. A., Sutton, L. E., & Hopkins, B. G. (2020). Nitrogen release rates from slow-and controlled-release fertilizers influenced by placement and temperature. *PLoS One*, *15*(6), e0234544.

101. Rasal, A. S., Yadav, S., Yadav, A., Kashale, A. A., Manjunatha, S. T., Altaee, A., & Chang, J.-Y. (2021). Carbon quantum dots for energy applications: a review. *ACS Applied Nano Materials*, *4*(7), 6515–6541.

102. Romanelli, A., Soto, D. X., Matiatos, I., Martínez, D. E., & Esquius, S. (2020). A biological and nitrate isotopic assessment framework to understand eutrophication in aquatic ecosystems. *Science of the Total Environment*, *715*, 136909.

103. Saraswat, S. K., Mustafa, M. A., Ghadir, G. K., Kaur, M., Lozada, D. F. G., Al-Ani, A. M., Alshahrani, M. Y., Abid, M. K., Jumaa, S. S., & Alhameedi, D. Y. (2024). Carbon quantum dots: A comprehensive review of green Synthesis, characterization and investigation their applications in bioimaging. *Inorganic Chemistry Communications*, 112279.

104. Sharma, B., Shrivastava, M., Afonso, L. O. B., Soni, U., & Cahill, D. M. (2022). Zinc-and magnesium-doped hydroxyapatite nanoparticles modified with urea as smart nitrogen fertilizers. *ACS Applied Nano Materials*, *5*(5), 7288–7299.

105. Skorupka, M., & Nosalewicz, A. (2021). Ammonia volatilization from fertilizer urea—a new challenge for agriculture and industry in view of growing global demand for food and energy crops. *Agriculture*, *11*(9), 822.

106. Sourati, R., Sharifi, P., Poorghasemi, M., Alves Vieira, E., Seidavi, A., Anjum, N. A., Sehar, Z., & Sofo, A. (2022). Effects of naphthaleneacetic acid, indole-3-butyric acid and zinc sulfate on the rooting and growth of mulberry cuttings. *International Journal of Plant Biology*, *13*(3), 245–256.

107. Standardization, I. O. for. (2016). *ISO 18644 Fertilizers and Soil Conditioners, Controlled-Release Fertilizer, General Requirements*. ISO Geneva, Switzerland.

108. Stangoulis, J. C. R., & Knez, M. (2022). Biofortification of major crop plants with iron and zinc-achievements and future directions. *Plant and Soil*, *474*(1), 57–76.

109. Stanton, C., Sanders, D., Krämer, U., & Podar, D. (2022a). Zinc in plants: Integrating homeostasis and biofortification. *Molecular Plant*, *15*(1), 65–85.

110. Stanton, C., Sanders, D., Krämer, U., & Podar, D. (2022b). Zinc in plants: Integrating homeostasis and biofortification. *Molecular Plant*, *15*(1), 65–85.

111. Stiles, L. I., Ferrao, K., & Mehta, K. J. (2024). Role of zinc in health and disease. *Clinical and Experimental Medicine*, *24*(1), 38.

112. Suganya, A., Saravanan, A., & Manivannan, N. (2020). Role of zinc nutrition for increasing zinc availability, uptake, yield, and quality of maize (Zea mays L.) grains: An overview. *Commun. Soil Sci. Plant Anal*, *51*(15), 2001–2021.

113. Sun, G., Wang, M., & Dong, Y. (2023). Enhanced-Efficiency Nitrogen Fertilizers Coated with Sulfur, Inhibitor, and Epoxy Resin: Preparation and Effects on Maize Growth and Nitrogen Utilization. *Journal of Soil Science and Plant Nutrition*, *23*(3), 4091–4103.

114. Sun, Y., Zhang, M., Bhandari, B., & Yang, C. (2022). Recent development of carbon quantum dots: biological toxicity, antibacterial properties and application in foods. *Food Reviews International*, *38*(7), 1513–1532.

115. Tian, H., Zhang, L., Sun, X., Cui, J., Dong, J., Wu, L., Wang, Y., Wang, L., Zhang, M., & Liu, Z. (2022). Self-healing modified liquefied lignocellulosic cross-linked bio-based polymer for controlled-release urea. *Industrial Crops and Products*, *186*, 115241.

116. Timilsina, A., Bizimana, F., Pandey, B., Yadav, R. K. P., Dong, W., & Hu, C. (2020). Nitrous oxide emissions from paddies: understanding the role of rice plants. *Plants*, *9*(2), 180.

117. Umair Hassan, M., Aamer, M., Umer Chattha, M., Haiying, T., Shahzad, B., Barbanti, L., Nawaz, M., Rasheed, A., Afzal, A., & Liu, Y. (2020). The critical role of zinc in plants facing the drought stress. *Agriculture*, *10*(9), 396.

118. Vejan, P., Khadiran, T., Abdullah, R., & Ahmad, N. (2021). Controlled release fertilizer: A review on developments, applications and potential in agriculture. *Journal of Controlled Release*, *339*, 321–334.

119. Vercelli, B., Donnini, R., Ghezzi, F., Sansonetti, A., Giovanella, U., & La Ferla, B. (2021). Nitrogen-doped carbon quantum dots obtained hydrothermally from citric acid and urea: The role of the specific nitrogen

centers in their electrochemical and optical responses. *Electrochimica Acta*, *387*, 138557.

120. Wang, L., Kelly, P. V, Ozveren, N., Zhang, X., Korey, M., Chen, C., Li, K., Bhandari, S., Tekinalp, H., & Zhao, X. (2023). Multifunctional polymer composite coatings and adhesives by incorporating cellulose nanomaterials. *Matter*, *6*(2), 344–372.
121. Wang, Z.-H., & Li, S.-X. (2019). Nitrate N loss by leaching and surface runoff in agricultural land: A global issue (a review). *Advances in Agronomy*, *156*, 159–217.
122. Widiyandari, H., Al Ja'farawy, M. S., Parasdila, H., Astuti, Y., Arutanti, O., & Mufti, N. (2023). Temperature impact on the morphological evolution of nitrogen-doped carbon quantum dot-decorated zinc oxide and its influence on highly efficient visible-light photocatalyst. *Physica B: Condensed Matter*, *669*, 415293.
123. Wu, D., Zhang, Y., Dong, G., Du, Z., Wu, W., Chadwick, D., & Bol, R. (2021). The importance of ammonia volatilization in estimating the efficacy of nitrification inhibitors to reduce N2O emissions: A global meta-analysis. *Environmental Pollution*, *271*, 116365.
124. Xu, X., Ray, R., Gu, Y., Ploehn, H. J., Gearheart, L., Raker, K., & Scrivens, W. A. (2004). Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *Journal of the American Chemical Society*, *126*(40), 12736–12737.
125. Yaru, G. E., Yu, L. I., Yuanjie, D., Mingrong, H. E., & Xinglong, D. A. I. (2024). Effect of synergistic urea by nitrification inhibitor coated with resin on wheat growth and soil nitrogen supply. *Pedosphere*, *34*(5), 960–970.
126. Younas, N., Fatima, I., Ahmad, I. A., & Ayyaz, M. K. (2023). Alleviation of zinc deficiency in plants and humans through an effective technique; biofortification: A detailed review. *Acta Ecologica Sinica*, *43*(3), 419–425.
127. Zhang, L., Tian, H., Zhang, M., Wu, L., Guo, W., Fang, F., Sun, X., Zhong, Z., Du, L., & Liu, Z. (2022). Preparation and properties of bio-based polyurethane controlled release urea coating with photosensitivity. *ACS Omega*, *7*(10), 8558–8569.

128. Zhang, L., Yang, X., Yin, Z., & Sun, L. (2022). A review on carbon quantum dots: Synthesis, photoluminescence mechanisms and applications. *Luminescence*, *37*(10), 1612–1638.

129. Zhao, H., Liu, G., You, S., Camargo, F. V. A., Zavelani-Rossi, M., Wang, X., Sun, C., Liu, B., Zhang, Y., & Han, G. (2021). Gram-scale synthesis of carbon quantum dots with a large Stokes shift for the fabrication of eco-friendly and high-efficiency luminescent solar concentrators. *Energy & Environmental Science*, *14*(1), 396–406.

130. Zhao, J., & Fan, Z. (2020). Using zinc ion-enhanced fluorescence of sulfur quantum dots to improve the detection of the zinc (II)-binding antifungal drug clioquinol. *Microchimica Acta*, *187*, 1–8.

131. Zhao, X., Qi, X., Chen, Q., Ao, X., & Guo, Y. (2020). Sulfur-modified coated slow-release fertilizer based on castor oil: synthesis and a controlled-release model. *ACS Sustainable Chemistry & Engineering*, *8*(49), 18044–18053.

132. Zhou, G., Chen, J., Wen, L., & Liu, J. (2024). Carbon quantum dots and N-doped g-C3N4 co-decorated ZnO nanorod arrays for enhanced photoelectrochemical water oxidation. *Catalysis Letters*, *154*(5), 2057–2066.

133. Zhu, J., Wu, C., Cui, Y., Li, D., Zhang, Y., Xu, J., Li, C., Iqbal, S., & Cao, M. (2021). Blue-emitting carbon quantum dots: Ultrafast microwave synthesis, purification and strong fluorescence in organic solvents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *623*, 126673.

134. Zhu, L., Chen, L., Gu, J., Ma, H., & Wu, H. (2022). Carbon-based nanomaterials for sustainable agriculture: their application as light converters, nanosensors, and delivery tools. *Plants*, *11*(4), 511.

135. Zulfiqar, U., Hussain, S., Maqsood, M., Ishfaq, M., & Ali, N. (2021). Zinc nutrition to enhance rice productivity, zinc use efficiency, and grain biofortification under different production systems. *Crop Science*, *61*(1), 739–749.