

**DEVELOPMENT OF DUAL PURPOSE BIO-BASED
POLYMER COATED UREA FERTILIZER:
CONTROLLED NITROGEN RELEASE AND TAILORED
ZINC SUPPLY**



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(2024)

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

Master of Science in

Environmental Sciences

Supervisor: Dr. Muhammad Ansar Farooq

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Approval Certificate

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“Development of Dual Purpose Bio-Based Polymer Coated Urea Fertilizer: Controlled Nitrogen Release and Tailored Zinc Supply”

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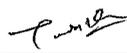
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List of Abbreviations

NH ₃	Ammonia gas
AAS	Atomic Absorption Spectroscopy
BPCU	Bio-polyurethane Coated Urea
BET	Brauner-Emmett-Teller
CO ₂	Carbon dioxide
CRU	Controlled Release Urea
DCU	Dual-Coated Urea
EENFs	Enhanced Efficiency Nitrogen Fertilizers
FTIR	Fourier Informed Infrared
GWP	Global warming potential
GHGs	Greenhouse gases
MSN	Mesoporous Nanosilica
NO ₃ ⁻	Nitrate
NO ₂ ⁻	Nitrite
N ₂	Nitrogen
N ₂ O	Nitrous oxide
SEM-EDX	Scanning Electron Microscopy-Energy Dispersive X-ray
TKN	Total Kjeldahl Nitrogen
XRD	X-ray Diffraction
Zn	Zinc
ZnUE	Zinc Use Efficiency
ZnO	Zinc oxide
MSN@ZnO	Zinc oxide loaded Mesoporous nanosilica

Abstract

The increasing population has led to a rise in global food demand, which has put immense pressure on the agricultural soils to boost crop yield. This has urged farmers to resort to the utilization of excessive amounts of urea fertilizer to match the demand. However, highly volatile and soluble nature of urea has resulted in various forms of environmental pollution, leading to low Nitrogen use Efficiency (NUE). Moreover, Zn deficiency in soil has also emerged as a growing concern, causing low crop productivity and nutritional value which eventually translates to Zn malnutrition in humans. This study aimed to address both the issues by developing a Zn fortified, controlled release urea fertilizer. A dual-coated urea was formulated featuring an inner coat of bio-based polyurethane and an outer coat of ZnO loaded mesoporous nanosilica particles (MSN@ZnO) embedded in a hydrogel matrix. FTIR, XRD, BET and SEM-EDX were employed to ensure successful synthesis of MSN and MSN@ZnO. Then to assess and optimize the N release of the bio-polyurethane coated urea (BPCU) and dual-coated urea (DCU), water and sand column release tests were performed. The results of Total Kjeldahl Nitrogen (TKN) revealed that coating urea, with both the layers decreased its nitrogen release. In water release tests, BPCU and DCU gave a cumulative N release of 71% and 68% respectively on day 28 and in sand column release tests BPCU and DCU gave a release of 73% and 68% respectively on day 28. This indicated viability of the coatings. Then to test for Zn release from DCU, Atomic Absorption Spectroscopy (AAS) was performed, the results of which demonstrated a burst release of Zn in water, whereas, in sand a prolonged micronutrient release profile was observed, extending up to 7 days. Hence, this study demonstrated a viable solution to combat two of the most concerning issues related to agriculture. For prospects, it is recommended to study the biodegradability of the coatings done and to assess the release of N and Zn from coated urea fertilizer in real-world environment.

Keywords: Low NUE, Urea Losses, BPCU, DCU, MSN

INTRODUCTION

1.1 Background

As the arable land shrinks around the globe, farmers are grappling with boosting the crop productivity on the remaining land to fulfil the global food demands. This challenge urges farmers to adopt unsustainable agricultural practices where excessive inputs are fed to the land, leaving it degraded and exhausted, while contributing to water pollution (Dhankhar & Kumar, 2023). Excessive inputs include overuse of pesticides and fertilizers where urea is the most used fertilizer (Hao et al., 2021). This issue, though prevalent worldwide has affected the developing nations the most. In Pakistan, a huge challenge in agricultural practices is the lack of awareness and education among farmers especially pertaining to the proper use of fertilizers. Where, N is applied abundantly as compared to Potassium (K) and Phosphorus (P) this in turn creates an imbalance (Wakeel & Ishfaq, 2016). This irrational use has become a norm in farming traditions, partly because farmers are not adequately informed about the adverse effects of nitrogen imbalance or the benefits of using fertilizers in a calculated manner (Wakeel, 2015). As a result, urea is often applied unwisely, without considering the specific nutrient needs of the soil or the crop. Many farmers hold the misconception that using more urea translates to better crop yields and thriving fields. This belief stems from the initial visible benefits of nitrogen application, such as rapid plant growth and lush fields. However, this perception is misleading, as excessive use of urea often leads to loss of yield, soil degradation, and environmental damage (Motasim et al., 2024). Over time, this practice not only reduces environmental health but also leads to economic inefficiencies as well, as farmers feel motivated to spend more on fertilizers than necessary in order to achieve sufficient output.

The issue with conventional urea is that the bioavailable forms of Nitrogen (N) which are NO_3^- and NO_2^- formed from ammonium (NH_4^+) are highly volatile and soluble in nature which causes it to diffuse rapidly through the soil leading to the aforementioned environmental issues. Since the rate of N release is rapid as compared to the N assimilation rate of plants, it leads to excessive and unused urea moving throughout the ecosystems unchecked (Swify et al., 2023). The environmental issues that arise from the unhindered movement of NO_3^- and NO_2^- in the environment are, the volatilization of ammonia gas, and climate change due to the emission of nitrous oxide (N_2O). Also,

water pollution is another issue, as the excessive nitrates (NO_3^-) and nitrites (NO_2^-) end up in stagnant water bodies causing eutrophication, causing them to leach down into the groundwater (Tyagi et al., 2022). According to (Anas et al., 2020) Nitrogen Use Efficiency (NUE) is 30.2 to 53.2%. The losses can go up to 70% of the total available N. So, low NUE leads to huge urea losses, serving as a significant nuisance for the environment.

Another agricultural issue in the context of Pakistan that runs in parallel to N losses is micronutrient deficiencies mainly zinc (Zn) in soils and consequently in people (Rehman et al., 2020). Lack of Zn in soils leads to a detrimental effect on the crops resulting in stunted growth, decreased yield, and lowered nutritional value (Khan et al., 2021). The soils of Pakistan are inherently calcareous and low in organic matter which exacerbates the issue of Zn deficiency as the Zn does not become bioavailable due to these factors (Younas et al., 2022). This, in turn, leads to the population becoming Zn deficient as majority of the Pakistani population solely depends on staple crops to fulfil their nutritional requirements. Zn malnutrition can be a leading cause of various ailments such as stunted growth, impaired immunity, birth-related issues, etc. (Praharaj et al., 2021).

To overcome the issue of urea losses, Enhanced Efficiency Nitrogen Fertilizers (EENF) can be employed. These EENFs are specifically designed to hamper the sudden release of N, increasing productivity to the point where crop nutrient demands are adequately met (Dimkpa et al., 2020). Moreover, incorporating Zn in EENF can prove to be very beneficial, offering an intricate and all-encompassing approach to addressing these challenges.

EENF can be classified into various types, namely inhibitors, low solubility urea compounds and Controlled Release Urea (CRU) (Swify et al., 2023b). CRU offers various advantages over the others. CRU has a better N release profile as the release of N from CRU is in line with the plants' metabolic needs, this in turn does not necessitate frequent applications (Melara et al., 2024). Therefore, reducing the economic burden on the farmers.

CRU can be further divided into Coated Urea Fertilizers and Matrix-based Fertilizers. In recent times, coated urea has become the focus of the scientific community, accounting for more than 95% of the total slow-release fertilizers (Fu et al., 2018) thus,

instigating the formulation of many coating layers. Depending upon the requirement of the specific area, coated urea is engineered using various types of coating materials such as Inorganic materials and organic materials. The coating upon the urea granule creates a physical barrier preventing direct environmental exposure. So, when the CRU is exposed to water in the soil, for a steady N supply, a diffusion mechanism comes into play (Kassem et al., 2024). This causes the water to gradually seep into the layer and dissolve the urea granule followed by a gradual urea supply upon overcoming the osmotic pressure created inside (Azeem et al., 2014). This whole process takes time, and the gradual urea supply ensures the enhancement of NUE, this in turn prevents urea losses and abates environmental issues generated.

To counter the Zn deficiency in soils, CRU in composite with Zn can be synthesized which can serve as a single solution for both of the problems. Mostly, Zn in bulk form is coated onto the urea granules using various binders such as molasses, beeswax, honey, etc. (Mustafa et al., 2022). In recent times, integrating nanotechnology in agriculture has seen a rise thus, incorporating Zn nanoparticles because of their efficient uptake by the plants is a far better option.

1.2 Significance

Extensive studies have been conducted on CRU for the past several decades. However, only a small number of studies have focused on dual coated urea fertilizers with embedded Zn. Moreover, loading Zn nanoparticles in Mesoporous Nanosilica (MSN) as a Zn delivery system to soil has never been explored. Also, as Pakistan is a focal point when it comes to the issue of urea losses and Zn deficiency in soil and the people (Rehman et al., 2020). Therefore, Zn incorporated CRU would prove to be a step towards introducing sustainable agricultural practices in Pakistan.

CRU would be synthesized using cotton stalks which is an abundantly produced agricultural waste in Pakistan. The first layer would utilize the cotton stalks to formulate bio-polyurethane, and the second layer would feature a hydrogel layer with Zn loaded MSN. This composite fertilizer would prevent excessive urea losses which would in turn reduce the number of urea application required becoming less of a burden on farmers. Also, the steady N delivery system provided by the dual layers can improve crop yield. Furthermore, Zn supply to the soils can also contribute to boosting the crop productivity and so, on the whole this can help in meeting the national food demands.

Also, according to (“National Nutrition Survey 2018 Key Findings Report,” 2018) 22.1% of Pakistani population is deficient in Zn. So, incorporation of Zn would add more nutritional value to the crops which would eventually lead to the correction of Zn deficiency in Pakistani population as well.

1.3 Objectives

The objectives of the study are as follows:

- i) Synthesize mesoporous nano-silica (MSN) particles loaded with essential micronutrient Zn in the form of Zinc oxide (ZnO) (MSN@ZnO).
- ii) Develop double enveloped controlled release urea fertilizer using bio-based polyurethane as an inner coat and MSN@ZnO embedded in hydrogel as an outer coat.
- iii) Estimate & optimize nutrient release (N, Zn) rate of the developed product.

CHAPTER 2

LITERATURE REVIEW

2.1 Unsustainable Agricultural Practices: Global and Pakistan Perspective

The agricultural sector has long been the backbone of global food production. Although, it contributes to about 4.33% of the global GDP, it still falls short to keep up with the exponentially growing world population (World Bank, 2023). According to the data by World Bank, the arable land (hectare per person) has seen a steady decline. In the year 2000 the arable land (hectare per person) was 0.22 whereas in 2021 the arable land (hectare per person) fell to 0.18 (World Bank, 2021). This indicates that the food security issue would further intensify if prompt measures were not taken.

So, as arable land (hectare per person) is declining, farmers are faced with the challenge of making use of the land available to fulfil global food demand. This situation pressurizes farmers into adopting unsustainable practices for increasing crop productivity (Araújo et al., 2022). Those practices include monocropping, excessive use of water, pesticides and/ or fertilizers.

This problem is more prevalent in developing nations (Rehman et al. 2022). As in these countries the agriculture sector is an integral part of the country's economy and food security. Pakistan is a prime example of this challenge. Agriculture sector of Pakistan contributes to about 22.9% into the countries total GDP (GOP, 2023). This number indicates the pivotal role that agriculture plays in the country's flailing economy.

Data sourced from World Bank showcase that for the past many years Pakistan has seen many fluctuations in the annual growth in the sectors of Agriculture, forestry, and fishing, from being 6.1% in 2000 to a sharp decline of 2.3% in 2023 (World Bank, 2023). Also, the arable land of Pakistan has declined from 0.2 to 0.13 in the past 23 years (World Bank, 2021). Meanwhile, the population data show that the population has risen to almost 251 million in 2024 from 154 million in 2000 (Worldometer, 2023). These statistics demonstrate that Pakistan is moving towards a future where the challenge of food security will further intensify.

Now, farmers of Pakistan feel the pressure to meet the national food demands due to which they turn towards unsustainable practices which includes excessive use of fertilizers (Aslam et al., 2021). As due to lack of awareness rather than using a strategic approach, farmers equate the excessive use of fertilizers to increased yields. So, to boost crop production, farmers resort to applying excessive amounts of fertilizers, especially nitrogenous fertilizers, namely urea. According to (NFDC, 2024). N fertilizers are one of the most used fertilizers in Pakistan. This practice has led soils to become unresponsive to the urea fertilizer, as the soil becomes saturated with NO_3^- causing various types of environmental problems (Wang et al., 2022). Excessive NO_3^- eventually lead to low NUE as plants are unable to absorb and assimilate the NO_3^- as most of it gets lost in the environment. According to Elhassani et al. (2019), 40-70% of urea applied gets lost in the environment which results in low NUE, creating a deficiency of N in the soils which ultimately results in low crop productivity despite the addition of high urea dosage to fields.

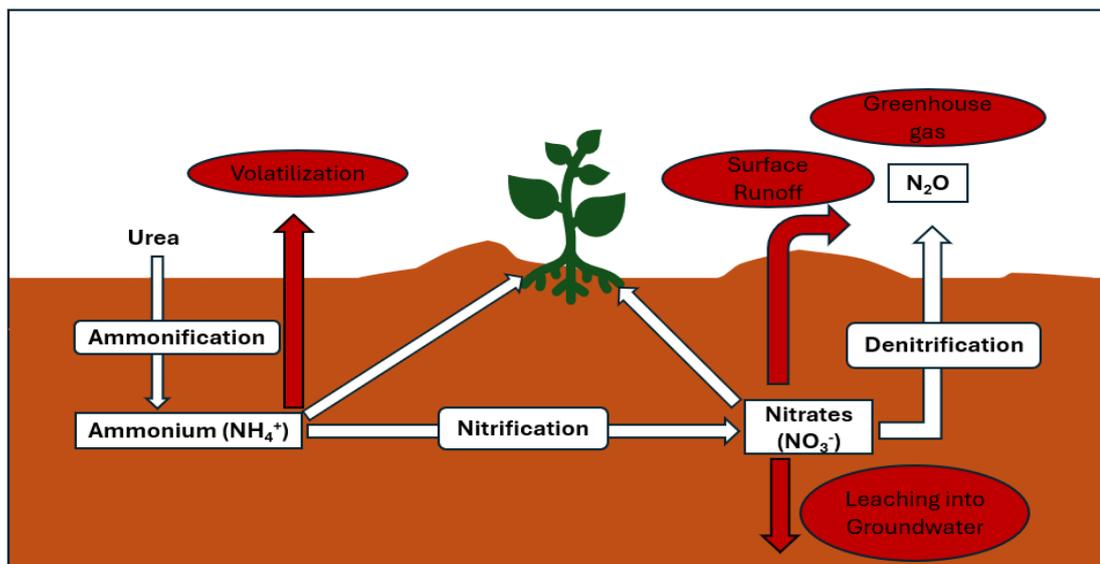


Figure 2.1: Urea loss pathways through nitrogen cycle. Urea is hydrolyzed into NH_4^+ then by the process of nitrification it is converted to NO_3^- , then finally denitrified into N_2O . The sources of nitrogen losses are volatilization (emission of NH_3), entering of NO_3^- in water bodies through surface runoff, NO_3^- leaching in ground water, dissipation N_2O after being denitrified. Adopted from (Motasim et al., 2024)

2.2 Challenges with Conventional Urea Fertilizer

Urea is the most commonly used nitrogenous fertilizer that, however, is characterized by high volatility and solubility in the agricultural environment (Tapia-Hernández et

al., 2022). Urea when applied to the soil undergoes immediate hydrolysis to transform to NH_4^+ for which the enzyme involved is urease. This NH_4^+ is then subjected to nitrification which is a biological process that involves conversion of NH_4^+ to NO_2^- and then to NO_3^- by soil microorganisms (Matczuk & Siczek, 2021). NO_3^- dissolve easily in water, and this results into its unchecked movement along ecosystems, eventually ending up in water bodies (Klimasmith & Kent, 2022).

Highly mobile nature of NO_3^- results in its leaching, leading to a loss of N which is not only a problem due to its unavailability to the crops but also leads to problems such as water pollution and water bodies becoming over-supplemented with nutrients, causing eutrophication (D. Guo et al., 2024).

Furthermore, the rate of NO_3^- uptake does not match with the NO_3^- production. This results in a negative balance of N. Owing to the urea's soluble nature, all of the N is released in early stages when plants need it the least, leaving none for the vegetative stage (Mansouri et al., 2023). This imbalance is a major cause of low NUE. This results in low yields and pollution; due to losses of N by volatilization, leaching and denitrification (Kumar et al., 2023). There is therefore a need to address these challenges in order to enhance the use of urea and sustainable agriculture. The N losses occur through various pathways as identified in Figure 2.1. Pathways through which urea is wasted are as follows:

2.2.1 Volatilization: N based fertilizers, especially urea when applied to the soils, the N is transformed chemically as well as biologically and in the process a lot of N is lost. By a process called hydrolysis, urea, when applied, dissolves in water and soil urease enzymes converts it in NH_4^+ . NH_4^+ is also a plant available N; however, it is very unstable in environment. NH_4^+ is also soluble in water and under conditions of low pH or in acidic lands, or high temperatures it tends to undergo a process called volatilization whereby it gets converted to NH_3 gas (NH_3) (Skorupka & Nosalewicz, 2021). The volatilization of NH_3 has the following problems: When NH_3 is released into the atmosphere, not only the nitrogen which should have been used by crops gone to waste, but NH_3 gas is also a nuisance. It is harmful when inhaled by both human and animals and affects the respiratory system of farmers in regions where there is intense farming (X. Ge et al., 2020). This problem is worse in areas with high temperatures because high temperatures cause hydrolyzing of the polymer and causes rapid release of NH_3

(Klimczyk et al., 2021). Likewise, it is established that soils with high pH levels encourage the transformation of NH_4^+ into NH_3 gas and thus increase volatilization. NH_3 gas is one of the sources of particulate matter ($\text{PM}_{2.5}$) which plays a significant role in air pollution, climate as well as human health (Wyer et al., 2022). When returned on to the land or the water bodies, it causes a decrease in pH levels of water and can result in eutrophication of water bodies which can affect the balance of life and leads to reduced species diversity.

2.2.2 Leaching into groundwater: As NO_3^- are soluble in water they are leached down into lower layers of soil and even aquifers (Matse et al., 2024). This leaching causes considerable loss of valuable nitrogen which is meant to be taken up by the crops and instead, environmental and public health gets impacted. The problem of high NO_3^- concentration in groundwater arises when these compounds move from the sub-surface to the human food chain, particularly in the rural areas where wells are common sources of water supply. Intake of drinking water with high concentration of NO_3^- results in various health impacts on humans depending on their status (Bijay-Singh & Craswell, 2021b). In adults the ingestion of NO_3^- leads to various ailments. Long-term also has been linked with serious states like thyroid disorders and some forms of cancer (Picetti et al., 2022).

Children who are most vulnerable to water containing NO_3^- are those below six months old because their systems easily convert NO_3^- to NO_2^- . NO_2^- affect the ability of the blood to transport oxygen through the interaction with hemoglobin, which results in a disease called methemoglobinemia, also known as “blue baby syndrome” (Choudhary et al., 2022). This condition lowers the amount of oxygen getting to tissues in the body leading to cyanosis, breathing problems and if not treated can cause death (Ishaq et al., 2022). The blue baby syndrome is a very real problem in areas of high agriculture use of urea, coupled with high rain or irrigation practices.

2.2.3 Surface run-off: The NO_3^- from the agricultural fields which are not taken up by the plants can become a part of surface run-off, during the rainy season or periods of high irrigation. This NO_3^- enriched water tends to drain to lentic systems which includes ponds, lakes and reservoirs. These water bodies being still or slow flowing water systems, become the receptacles for these excessive nutrients and so set off a chain reaction of effects in the ecosystem, causing eutrophication (Akinnowo, 2023). A

process in which water bodies receive high concentrations of nutrients resulting in algal blooms (Dellero, 2020). The algae form a dense layer on the water surface and prevent light from reaching the submerged plants which play crucial roles in the water oxygen cycle and as a habitat for other aquatic life. After the algae die, the decomposition of those algae requires a significant amount of dissolved oxygen in the water causing hypoxia or oxygen depletion. Such low oxygen levels form “dead zones,” regions in which many sea organisms cannot exist (P.C et al., 2020). Endangered fish, amphibians, and invertebrates either cannot breathe or must move due to the water pollution and therefore lead to biotic crisis. It also influences water quality where water becomes unfit for use for drinking, recreation or for supporting agriculture activities (Geletu, 2023). Toxin-producing algal blooms endanger public health as they lead to water pollution affecting drinking water sources and lead to diseases in humans and animals.

2.2.4 Denitrification: Excessive NO_3^- in the soil are not just lost nutrients but also play a significant role in contributing to climate change through the nitrogen cycle (IPCC, Climate Change 2013: The Physical Science Basis, 2014). When NO_3^- accumulate in the soil, they become substrates for denitrifying bacteria. These microorganisms perform a process called denitrification, where NO_3^- are reduced to gaseous nitrogen compounds, including nitrous oxide (N_2O) (Y. Zhang et al., 2022). N_2O is a highly potent greenhouse gas (GHG) with a global warming potential (GWP) approximately 273 times greater than carbon dioxide (CO_2) over a 100-year time scale (Xia et al., 2021). Once released into the atmosphere, N_2O contributes to the greenhouse effect by trapping heat, exacerbating climate change. This means even small emissions of N_2O can have a large impact on global warming.

The excessive application of urea and other nitrogen-based fertilizers in agriculture significantly increases the availability of NO_3^- in the soil, amplifying the risk of N_2O emissions. This makes excessive urea use a key driver of agricultural contributions to climate change.

2.3 Micronutrient Deficiencies around the Globe

Another issue that is concurrent with N losses is micronutrient deficiencies in soils. The deficiencies of micronutrients such as Iron, Zn, molybdenum, copper, Boron etc. can lead to low crop production and nutritional value (Assunção et al., 2022). Therefore, when humans consume them, it affects their health as well. These micronutrients play

an important role in plant and human metabolism. They can help plants with proper growth and development as they contribute to key metabolic functions such as enzyme activation, photosynthesis, reproduction etc. (Jatav et al., 2020). These micronutrients also help plants become resistant to pests and diseases and also improve plants' ability to better absorb and assimilate nutrients. In humans, these micronutrients are equally important as plants as they aid in maintaining overall health. They facilitate key functions, needed for survival and upholding fitness such as energy production, DNA synthesis etc. They also help in improving immunity and cognitive function and development.

So, low levels of these micronutrients impair plant health and result in creating malnutrition in humans as well. From among these deficiencies, the shortfall of some micronutrients is more serious than others because they are more prevalent in the world. According to Graham (2008) the prevalence of various micronutrient deficiencies in soils is that 49% are deficient in zinc (Zn), 31% deficient in boron (B), 15% deficient in molybdenum (Mo), 14% deficient in copper (Cu), 10% deficient in manganese (Mn) and 3% deficient in iron (Fe). This data shows that Zn deficiency is the most concerning as it is widespread as compared to the other micronutrients. This causes 17.3% of the world population to lack in serum Zn, according to Hacisalihoglu (2020). Mainly Asian and African countries suffer the most with Zn deficiency in soil and humans and from among them South Asian belt consisting of India and Pakistan show prominent signs of it.

2.3.1 Zinc Deficiency in Pakistan

As the arable land shrinks in comparison to population growth of Pakistan farmers struggle to maintain a steady food supply. In order to feed the growing population, farmers turn towards unsustainable agricultural practices such as monocropping, over-tillage etc. as they grapple to increase crop production. As farmers focus on quick and immediate returns, practices like monoculture, which involves planting of a single crop on a piece of land for several consecutive seasons are practiced. However, monocropping has adverse effects on the soils as it exhausts a specific nutrient because the cultivation of a single crop reduces the chances of nutrient intake by the soil and hinders natural soil recycles (Belete & Yadete, 2023).

Also, over tillage is used in the preparation of the soil for planting among other practices. Though this enhances soil aeration and ease in seed bed preparation, high intensity tillage reduces the formation and stability of soil structure, enhances compaction and erosion and reduces the organic matter content of the soil (Lv et al., 2022). These practices reduce the quality of the soil over a period of time. While soils are being stretched to the limit, their ability to support crop growth is diminished as the nutrient holding capacity of the soil decreases due to over tillage (Bechmann & Bøe, 2021).

One of the worst effects of this overexploitation is that micronutrient deficiencies have become apparent, especially Zn deficiency. Zn is vital nutrient for plant as well as human beings, it is an active part of enzymes as well as immune system (Vickram et al., 2021). In soils, Zn deficiency not only limits plant growth but also decreases the nutrient quality of the harvested produce (Khan et al., 2021b). According to (“National Nutrition Survey 2018 Key Findings Report,” 2018) the prevalence of Zn deficiency in Pakistan is 22.1%. Also, due to lack of awareness little to no Zn is added to the soils by the farmers which further amplifies the issue. Now, these unsustainable practices are a major reason why soils of Pakistan are faced with such an issue, other factors such as edaphic factors also play a role in creating low Zinc Use Efficiency (ZnUE) which ultimately leads to a deficiency in soils leading to Zn malnutrition in Pakistani population (Rehman et al., 2020). Those edaphic factors are:

2.3.1.1 Calcareous/ alkaline soils: The first and foremost important factor is the presence of consequential levels of calcium carbonate (CaCO_3) in soil, making it chalky and very alkaline. In Pakistan, around 80% of the soil is calcareous, fostering an environment that obstructs Zn’s availability in the soil (Ahmad et al., 2012). However, even if certain amount of Zn is found in the soil, they mostly react with the calcium carbonate, forming zinc carbonate (ZnCO_3), which is entirely insoluble in water (Singh et al., 2023). The formation of an insoluble compound in the soil, capitalizes the already depleted micro-nutrient necessary for root uptake. Another significant edaphic factor that unfavourably affects ZnUE is the high pH value of soils. The pH values in calcareous soils typically range from 7.5 to 8.5, which in turn, creates a disadvantageous condition for the solubility levels of Zn (Salinitro et al., 2020). With the pH further increasing, the Zn ions in the soil decrease as Zn tends to precipitate as insoluble complexes (Hacisalihoglu, 2020b) such as $\text{Zn}(\text{OH})_2$ at pH levels exceeding 7. A study

conducted by Natasha et al. (2021) concluded that Zn is more mobile and phytoavailable in acidic soils as opposed to alkaline soils.

2.3.1.2 Low organic matter: Unfortunately, the soils of Pakistan have low organic matter which is disastrous for plant growth and nutrient uptake (A. Ullah et al., 2020). It is noteworthy that organic matter act as natural chelating agent that is helpful in maintaining the solubility of Zn and make it available to be absorbed by the plants (Hoffland et al., 2020). In its absence, Zn is likely to precipitate and form compounds that are insoluble and, therefore, unavailable to crops. Furthermore, organic matter contains essential substances, for instance, humus and fluvic acids and these acids can make Zn more phytoavailable (Boguta & Sokołowska, 2020). With low organic matter, the soil fails to provide a buffering action to maintain Zn in plant-available forms, which worsens the state of Zn deficiency in plants.

2.3.1.3 Sodicity and Salinity: In Pakistan, the problem of salinity is primarily due to poor drainage and excess irrigation with salt-containing water (Syed et al., 2020). This badly affects the process of nutrient uptake, consequently obstructing plant growth (Ehtaiwesh, 2022). This condition obtrudes with the uptake of Zn as salt ions struggle to replace Zn ions present in the soil particles. According to research conducted by Dang et al. (2024) on rice plants, saline-sodic soils can limit Zn availability to the crop as it impacts photosynthesis and metabolism. Increased salt levels induce osmotic stress in plants (Hailu & Mehari, 2021). Therefore, exacerbating the repercussions of Zn deficiency, further decreasing ZnUE in soil. So, these factors cause the already deficient micronutrient to become unavailable to the plants which decreases the nutritional value of the crops. Hence, eventually translating into Zn malnutrition in humans.

2.4 Combatting the Issues of Low NUE and ZnUE

2.4.1 Addressing the Challenge of Low NUE

To counter the issue of N losses, EENF can be used. These fertilizers give a gradual release of urea which would ensure that the nutrient is supplied at a rate which is in sync with the plant's metabolic needs preventing excessive NO_3^- being dissipated into the environment causing pollution.

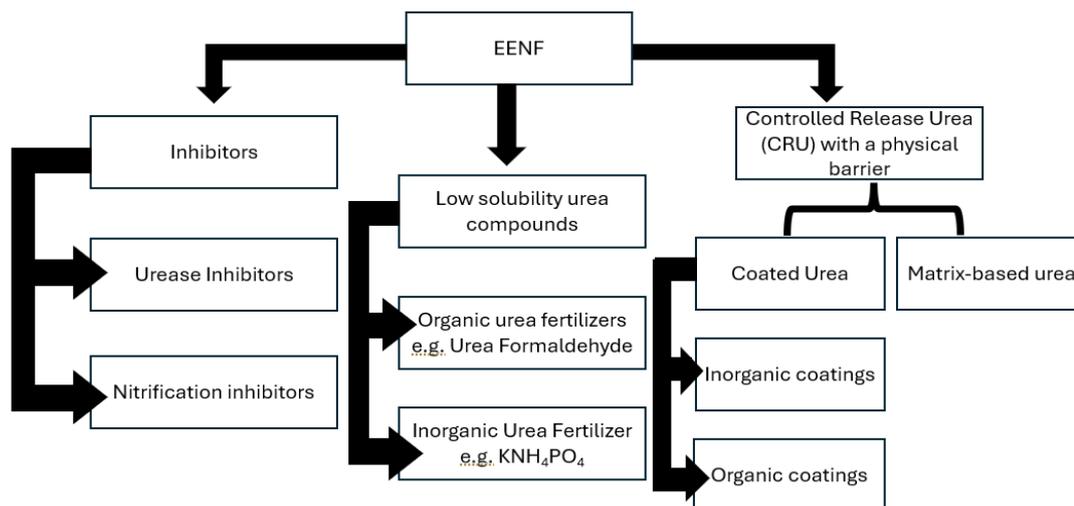


Figure 2.2: Classification of EENF. This diagram categorizes EENF into three main types: Inhibitors, low solubility urea compounds and CRU. It focuses on subcategories including urease and nitrification inhibitors, organic and inorganic low solubility urea fertilizers and CRU further divided into coated urea or matrix-based. Adopted from (Lapushkin et al., 2024).

Also, this method would alleviate the issue of highly volatile and soluble nature of urea fertilizer which would prevent N losses. Figure 2.2 shows classification of EENF. Thus, using EENF would increase NUE which would lead to better crop productivity and improved environmental health. There are certain types of EENF that can be used to prevent urea losses.

1) Inhibitors

a) Urease Inhibitors (UI)

When urea is added to the soil is broken down by urease enzyme into NH_4^+ and carbon dioxide. This process is known as urea hydrolysis which lead to high amounts of N losses as the NH_4^+ get converted into NH_3 gas by the process of volatilization which is then let off into the atmosphere. This causes reduced amount of N being available for the plants. So, when urease inhibitors are added into the soil, it reduces and delays the process of urea hydrolysis reducing N losses (Prasad & Shivay, 2021). This allows for N to penetrate deeper into the soil and get absorbed by the plants instead of getting lost into the environment. According to a study carried out in Pakistan, Dawar et al. (2021) assessed the effectiveness of biochar with UI on wheat crop, the results showed a better crop yield with an increase in biomass, grain yield and N uptake by 38%, 22% and 27% respectively. In another study done by Ullah et al. (2021) demonstrated the effectiveness

of using Gibberellic acid (GA₃) and UI, namely N-(n-butyl)thiophosphorictriamide (NBPT) on maize crop. Combination of both increased maize yield as compared to the control experiment.

b) Nitrification Inhibitors (NI)

Upon urea addition to soil, it gets converted into NH₄⁺ which is then transformed into NO₃⁻ by the action of microorganisms. At first Nitrosomonas convert NH₄⁺ into NO₂⁻ and then Nitrobacter bacteria transforms NO₂⁻ into NO₃⁻. NO₃⁻ being highly soluble are very mobile in nature so get lost in the environment being of no use of plants. NO₃⁻ are then readily converted to N₂O as well (Nardi et al., 2020). Nitrification inhibitors suppress the activity of the nitrifying bacteria mentioned above, this causes slow formation of NO₃⁻ which reduces N losses and increases NUE. Nitrapyrin, a type of nitrification inhibitor acts at an early stage and restricts the conversion of NH₄⁺ into NO₂⁻ (Woodward et al., 2021). In an experiment conducted on wheat crop by Dawar, Rahman, et al. (2021) demonstrated that application of Gibberellic acid (GA-K salt) along with Nitrapyrin significantly improved wheat yield biomass, grain yield and total N uptake by 31%, 37% and 44% respectively.

1) Low solubility Urea/ ammonium containing fertilizers

Low solubility urea compounds are the type of urea fertilizer which are slow to dissolve upon application as opposed to conventional urea. They control the release of urea by decreasing the interaction of the fertilizer with soil and also by inhibiting the microbe induced reactions (Lapushkin et al., 2024). These urea fertilizers are produced through various reactions and techniques such as polymerization etc. which renders them with low soluble nature. Also, some naturally existing compounds containing NH₄⁺ can also be classified as low solubility compound due to their strong interactions with other molecules present in the salt.

a) Low Solubility Organic Urea Fertilizer

This type of nitrogen-based fertilizers contains nitrogen in an organic form which has low water solubility. Examples include:

- **Urea Formaldehyde (UF)**

Urea formaldehyde is composed of a network system in which the urea molecules are cross-linked/ polymerized with formaldehyde is combined with formaldehyde. The release rate of N is dependent upon the level of polymerization. UF is made up of two types of fractions, which are Cold water insoluble fraction which releases N at a more slower pace due to the presence of long-polymer chains and hot water insoluble fraction which releases N readily (Guo et al., 2023). UF is mostly combined with a binder to be used as a slow-release fertilizer. Yamamoto et al. (2015) designed a nanocomposite slow-release urea fertilizer using paraformaldehyde and montmorillonite with various ratios using cold extraction technique. In another study Giroto et al. (2017) formed a urea and paraformaldehyde composite with different ratios and tested its release in water and soil. The composite with a ratio of Ur: Pf 0.5:1 and 1:1 showed a better release in water where only 20% and 25% of urea was solubilized respectively in 120 hours. In soil, volatilization of the composite was measured where is showed that it was less than 10% for Ur: Pf 1:0.5 in Red-yellow and Red oxisols on day 42 as compared to urea which was almost 60% in the same period.

- **Isobutylidene diurea (IBDU)**

IBDU is produced by the reaction of urea with isobutyraldehyde. Its release is mainly dependent on edaphic factors such as soil temperature, moisture and pH (Nardi et al., 2017). The hydrolysis process of IBDU is slow, making it a viable candidate for SRF. However, its use has become obsolete, use of IBDU was popular in late 20th century but now due to the introduction of various other forms of slow/ controlled release fertilizer its use has seen a decline.

- a) Low Solubility Inorganic Urea Fertilizers**

Some of the examples for low solubility inorganic urea fertilizer are KNH_4PO_4 and MgNH_4PO_4 also known as struvite (Azeem et al., 2014). The complex nature of interactions among the molecules of such fertilizers makes it a slow-release fertilizer.

- 1) Controlled Release Urea (CRU) with a physical barrier**

CRU with a physical barrier is designed to limit the exposure of the urea fertilizer to the external environment so that rate of chemical process such as volatilization,

nitrification etc. is reduced. This category includes coated urea fertilizers and also matrix-based urea fertilizers (Lawrencia et al., 2021).

a) Coated Urea Fertilizers

These fertilizers have a layer of coat around the urea core. The coating is designed using various materials such as polymers etc. which protects the urea core from volatilizing and solubilizing quickly into the atmosphere, decreasing N losses (Gülüt, 2024).

- **Inorganic coatings**

- **Sulfur**

Versatile nature of sulfur makes it an adequate control release agent for nitrogen. It plays an essential role in plant nutrition (Sharma et al., 2024). Hence, further supporting it to be used to coat urea especially areas where alkaline soils predominate. From 20th century till this date, many sulfur coatings have been tried and tested. A study was conducted by (Detrick, 1994) in which double layered coated urea was formulated by first spraying sulfur on the urea and then the second layer comprised of spraying the sulfur coated urea with diethylene glycol triethanolamine polyol and diisocyanate monomers. This study was expanded then by producing a triple coated urea. It had an inner layer formed by on-surface polymerization of certain monomers (4,4-diphenylmethane diisocyanate, triethanolamine and diethylene glycol polyols). The second layer was of molten sulfur and the final layer was made by on-surface polymerization of the previously mentioned monomers (Detrick, 1999). Sulfur coatings made its way into 21st century as well. (Liu et al., 2008) developed a sulfur coating that was modified by dicyclopentadiene. Both were blended at high temperatures and then the coated urea was tested in deionized water. (Mehmood et al., 2019) used a combination of two or three different materials, namely, sulfur, gypsum, bentonite and starch with paraffin wax as a binder. The sulfur and gypsum coated urea gave better results out of all combinations. (Ghumman et al., 2022) synthesized a novel, sulfur enriched urea fertilizer was formulated using a crosslinked copolymer that was made from sulfur and rubber seed oil. To coat the urea dip coating method was employed. The water release tests showed that 65% of nitrogen was released in 43 days when the coating thickness was 264 μ m.

- **Silica**

Silica has been used extensively for coating urea prills for the formulation of CRU, but silica is not used as a stand-alone coat, it is used as a filler mostly along with other materials to form a composite. (Li et al., 2016) spray coated a blend of polyol, stannous octoate, microcrystalline wax, SBA-15 and PAPI to form CRU. After coating, its release behaviour was checked in distilled water and characterization was done. The release tests showed that the addition of SBA-15 in comparison of the addition of SiO₂. When the coating ratio stood at 3.5% the product gave a release till day 80. (S. Zhang et al., 2017) created a CRU by coating it with a bio-based polyurethane derived from wheat straw which was then modified using Organosilicon and nano-silica to make the coat super hydrophobic. The developed product with 10% and 20% of Organosilicon and nano-silica component gave better results with a 7% coating material. The results demonstrated that on day 40, SBPCF10 and 20 gave a release of almost 40% and 60% respectively. (Sahu et al., 2022) conducted a study in which they developed jute grafted silica nanoring was coated around urea with egg white used as binder and the study varied the thickness of the coating material. The results demonstrated that CRU with a coating percentage of 9% and 14% showed the most controlled release with almost only 70% of N release in 60 days.

- **Clay**

Clays are often use in conjunction with other, mostly organic materials to coat urea fertilizer. Umar et al. (2022) developed a product with Zn nanoparticles and Zn fortified nano-bentonite clay. The results concluded that ZU1 & ZU2: Coated with 4% nano-bentonite and 2% ZnO NPs using vegetable oil and stearic acid, respectively released higher amounts of Zn. Whereas ZU3 & ZU4: Coated with 4% nano-bentonite and 2% ZnO NPs, stearic acid, paraffin oil, and paraffin wax respectively gave a prolong release of Zn. For N release, Zu3 and ZU4 gave the steadiest release of N in 15 days while ZU1 and ZU2 gave a rapid N release. Sitthisuwannakul et al. (2022) developed a tunable controlled release urea fertilizer (TCRU) with linseed oil-modified polyurethane resin and nanoclay. TCRU with 10% nanoclay fraction gave the best N release. In another study conducted by (S. Zhang et al., 2020) developed a dual layered SRF with a hydrophobic lignin-clay nanohybrid as an inner coat and an outer coat of highly water-absorbent polymer poly(acrylic acid) (PAA) forming a PLC-SRF. The results

demonstrated that using the PLC-SRF gave the best results with 70% of N being released on day 5.

- **Organic coatings**
 - **Organic synthetic polymer coatings**

Use of synthetic, non-biodegradable polymers especially the ones derived from petroleum-based products were common for coating urea in previous years. Commonly used coating materials include synthetic polymers, such as polyolefins, polysulfones, acrylic resin polyvinylidene chloride etc. (Yuan et al., 2022). Yang et al. (2012) formulated a polymer coated urea (PCU) using recycled polystyrene foam along with various sealants. Along with PCU, large tablet coated urea (LTPCU) was also formed. PCU with 7% coat with varying amounts of wax showed release of ~90% on day 42. LTPCU with a 3% coating and 15% polyurethane showed a very slow N release, a release of ~80% was observed on day 98. Akmal D et al. (2015) developed a polystyrene/ starch coated urea with varying ratios using a pan coating machine. The results of urea release (%) against time in days showed that the composite with PS/Starch of 3:1 demonstrated a better release with 45% of urea being release in 10 days. Many field trials were conducted using Polyolefin coated urea in previous years. Polyolefin coated urea was tested on different crops such as Cotton (D. Chen et al., 2007), Rice (Xu et al., 2012) and Sorghum (Szydełko-Rabska & Sowiński, 2014). However, petroleum-based coating proved to have many downfalls in terms of its effects on the environment. The coating done is non-biodegradable which could be toxic (Babar et al., 2016) and can get accumulated in the soil, which can in turn have several negative impacts on soil's health. These materials are extracted from non-renewable sources and often prove to be harmful to the environment. Using non-biodegradable polymers as a coating material can result in white pollution and can disrupt soil function (Beig et al., 2020). Although, some studies are still being conducted using synthetic polymers for coating urea purposes, like the following study conducted by Ge et al. (2024) in which they synthesized six varieties of coated urea, one of which was rock phosphate mixed with epoxy resin to coat urea where polyvinyl alcohol was used as a binder. The results demonstrated a very slow release of N which was ~70% on day 80. Cumulative release of NH₃ volatilization was also measured giving a value of 3.5% on day 40 as compared to conventional urea which was ~7%.

However, more focus has been shifted to organic, bio-based polymers now. Liu et al. (2018) formulated an elastic polyurethane coated urea (ECU) fertilizer using waste palm oil. The authors first epoxidized palm oil and then to obtain polyols, the resultant material was treated with HCl and methanol while heating it. The obtained polyols were then mixed with MDI and a drum machine was used to coat urea with polyurethane with 3%, 5% and 7% coat. To grant the formulated polyurethane with elastic/ swelling capabilities it was further processed with DBTDL, acetone and Acrylonitrile along with an initiator and then the urea was coated the same way as polyurethane coated urea (PU). The results revealed excellent swelling capabilities and cumulative nitrogen release was significantly slowed down in ECU as compared to PU. The results demonstrated a nutrient release that extended for up to 80 days as compared to PU whose release longevity was of 50 days. Jia et al. (2020) conducted a study in China where they utilized food leftovers, réchauffé and a mixture of both retrieved from a school canteen to formulate bio-based polyurethane. The food obtained was liquified and then polyols were extracted from it and reacted with a polyisocyanate. Coating was done using a rotary drum machine and a coat of 4%, 6% and 8% was done. The results revealed that 8% coating of polyurethane formulated using food leftovers performed the best with around 35% N cumulative release rate at day 14 whereas, polyurethane synthesized from réchauffé released about 55% of nitrogen in 14 days and a mixture gave a release of approximately 45% in the same amount of time. S. Chen et al. (2020) formulated a bio-based polyurethane using spend mushroom waste that was modified using nano-SiO₂ and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FAS) to increase its hydrophobicity (SBCU). The results showed a release of 70% on day 28.

- **Organic biopolymers**

- Starch**

- Pimsen et al. (2021) developed a starch-based slow-release fertilizer using nano zeolite in composite-chitosan/ sago starch-based biopolymer. The resultant product served as a multi-purpose CRU with water absorption capacity. The results revealed that the product can significantly control the release of urea, and it can hold significant amount of water as the size of the bead grew by 225.19% by weight within 16h of immersing in water. The urea release profile showed a release of almost 41% on day 14 for the product. Zafar et al. (2021) developed a controlled release urea by coating the prills using a fluidized bed with starch and polyvinyl alcohol (PVA) in combination with

acrylic acid (AA), citric acid (CA) and maleic acid (MA). Product with 2% Acrylic acid and Citric acid showed a release of 70.10% and 50.74% respectively and when tested on Spinach plant these two composites showed the best result with respect to various yield parameters. Swami et al. (2023) formulated a phosphate modified starch coated urea with eggshell nanoparticles. The results showed that almost 30 % of the nutrient was released in the initial ten days and the release was maintained for up to 60 days giving 90 % release.

Chitosan

Mohammadi et al. (2019) developed a CRU using sepiolite and chitosan with different ratios to form nanocomposite which were coated on urea using carboxymethyl cellulose powder as an organic glue along with water. To assess the release of the product, sand column and soil release tests were performed. Urea with 3:1 of clay to polymer content (C3P1U) showed the best result in soil column test where 75% of N was released on day 30, but in soil C1P3U showed the most controlled release with 50% release of N on day 30. In a study done by (Elhassani et al., 2023) Chitosan (CS) was blended with polyvinyl alcohol (PVA) (50/50, wt/wt) followed by the addition of lignin nanoparticles (LNPs) at various loadings (1, 2, 3, and 5 wt% LNPs). The viscous solution was coated on to urea with 2%, 4% and 7% coat by weight. The CRF with 7% coat gave the best release with 100% being release in 384 hours.

Lignin

Chen et al. (2022) formed various composites to coat urea which were lignin-based coated urea (LCU), lignin/paraffin coated urea (LPCU) and lignin/paraffin/epoxy resin composite coated urea (LPECCU) where lignin was dissolved in PEG-400 to form a lignin-based polyol which was then stirred with HDI to develop. The results showed that LPECCU with highest -CNO/-OH molar rate and a 7% coating material showed the best release profile where on day 50, 80% of N was released. Chen et al. (2022b) synthesized Carbon black and polysiloxane modified lignin-based polyurethane. The composite with 15% polysiloxane content and 7% coating rate showed a release longevity of 44 days. The product was also tested on cabbage where it showed better yield.

Mechanism of Nutrient Release from Coated Urea Fertilizers

The slow-release mechanism of urea release can be divided into three main phases (Azeem et al., 2014; Boonying et al., 2023; Lawrencina et al., 2021), that are highlighted in figure 2.3:

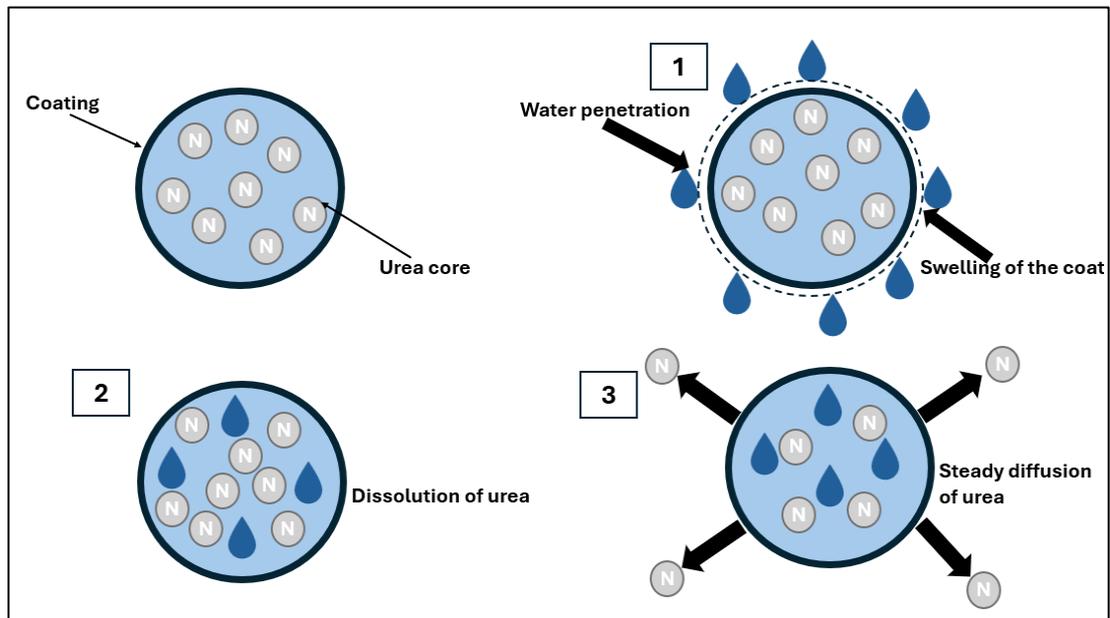


Figure 2.3: Nutrient release mechanism of CRU. This diagram shows the three stages of CRU. Phase 1: When water seeps into coating and it swells up. Phase 2: The water that gets absorbed solubilizes the urea core. Phase 3: The dissolved urea slowly diffuses through the semi-impervious covering into the surrounding soil. Adopted from (Boonying et al., 2023).

First phase: Water penetration and swelling of coated layer

When coated urea is added in water or applied to soil the water slowly starts to penetrate the coated granule. The water may find micro-cracks or holes to gradually seep through the semi-permeable barrier around the urea core. The penetration of water causes the coated layer to swell up and slightly increase its size. The degree of swelling of the coated layer depends upon various factors, such as: coating material used, coating thickness, environmental conditions.

Second phase: Dissolution of urea

As the coating swells up in response to the water penetration the absorbed water gradually makes its way to the urea core where it begins to dissolve. The rate of urea dissolution depends upon the rate of water being absorbed by the coated layer. As urea

dissolves, the solution formed exerts pressure on the internal walls of the coated layer. Due to the physical pressure exerted, the coating must be durable enough to withstand the force to resist the premature release or sudden release of the nutrient.

Third phase: Diffusion of urea

Finally, in the third phase of release, dissolved urea within the core of the granule diffuses through the coated layer and is released to the external environment along a concentration gradient. Diffusion rate depends on the coating's porosity, thickness, and adhesion to the substrate, and on the soil's moisture content, temperature, and biota. This controlled diffusion is in sync with the plant uptake thus reducing loss through leaching or volatilization, increased NUE and reduced effects on the environment.

b) Matrix Based CRU

Matrix based fertilizers mainly utilize the Urea fertilizer to be dispersed in a continuum which restricts its dissolution in the soil at a fast rate. Jayanudin et al. (2021) developed urea loaded chitosan-based microspheres. Urea was mixed in a solution of chitosan which was then put in oil which was then formed into an emulsion after which glutaraldehyde saturated toluene (GST) (crosslinking agent) was added into to form urea loaded chitosan microspheres. Volume ratio between continuous phase and dispersed phase of 8:1 showed a better N cumulative release which was 35% on day 30. Lusiana et al. (2024) synthesized a chitosan (CS) membrane modified with succinic acid (SA) and calcium ions (Ca^{2+}) using a sandwich model. A composite was formed with first layer being of CS and SA mixture with second layer of CS and SA-urea solution and third layer of CS and SA again. This whole SRF membrane was soaked with $\text{Ca}(\text{OH})_2$ solution with varying molarity. The product was tested in water and soil. CS-SA-U-Ca3 showed a better release of urea with almost 80% on day 20 in water. In soil, a better release profile was observed in which on day 30th less than 30% of urea was released. A study conducted by Kaavessina et al. (2021) synthesized a matrix-based urea in which urea powder was grounded to achieve micro-sized urea which was added into the melt of low molecular weight Polylactic acid (PLA) which was formed by polycondensation of lactic acid. Different loading of urea in matrix and molecular weights of PLA were assessed for their N release behaviours. Urea fraction release reached up to 80% in 336h. Niu et al. (2023) carried out a study in which sodium alginate (SA)/ urea hydrogel (SAUR) was formed. SA was dissolved in phosphate

buffer in which N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS) were added and then N,N,N',N'-Tetramethylethylenediamine (TEMED) was stirred in. Then, finally urea was added and mixed. The solution was left to dry in mould and was cut up in cubes. Various molar ratios of SA:urea were formed. SAUR with a molar ratio of SA:urea 1:0.625 showed aN content of 110mg/kg and a NO₃⁻ content of 130mg/ kg in 9 weeks.

2.4.2 Addressing Both Challenges with a Single Solution

Besides using Zn coated urea to fulfil the Zn deficient soils, Zn itself acts as a urease inhibitor (Sadiq et al., 2021) slowing down the conversion of urea into NH₃ gas, limiting losses. Crop yield can be increased by using Zn-coated urea as it can limit the hydrolysis of urea, acting as a urease inhibitor.

Irfan et al. (2018) conducted a study to assess the rate of Zn release from coated urea, ZnO along with several binders namely, water, molasses, paraffin oil and the combination of honeybee wax along with gum arabica. Different combinations were coated on urea using two different methods: slurry and wet coating. The results demonstrated a better, more controlled release for the urea coated using slurry method. ZnU5 (mixture of honeybee wax and gum) gave the most controlled release of 2ppm in 24h whereas, ZnU2 (mixture of honeybee wax, gum, paraffin oil and molasses) gave the most dramatic release which reached up to 13ppm in 12h. (Abdullah et al., 2022) formulated different Zn compounds blended with various binders which were molasses, paraffin oil and gelatine. They were coated onto urea using a fluidized bed. Synthesis, characterization, pot experiments, soil analysis, plant analysis and statistical analysis were conducted. The results revealed that a better plant yield was achieved using ZnO and gelatine composite and it also displayed a better micronutrient efficiency.

To further enhance the efficiency of Zn incorporated Urea, inclusion of nanotechnology in fertilizers have seen a rise. Umar et al. (2022) synthesized a product with Zn nanoparticles and Zn fortified nano-bentonite clay. The results showed that ZU1 & ZU2 that was coated with 4% nano-bentonite and 2% ZnO NPs using vegetable oil and stearic acid, respectively released higher amounts of Zn as compared to other composites. While ZU3 & ZU4 that were coated with 4% nano-bentonite and 2% ZnO NPs, stearic acid, paraffin oil, and paraffin wax respectively gave a prolong release of Zn. For N release, Zu3 and ZU4 gave the steadiest release of N in 15 days while ZU1

and ZU2 gave a fast N release. Dimkpa et al. (2022) synthesized a unique Zn coated urea nanofertilizer using various capping agents to stabilize Zinc. Capping agents used for this study were N-acetyl cysteine (NAC) and sodium salicylate (SAL); NAC and urea; or SAL and urea. The products were tested on Sorghum crop and the parameters tested were plant biomass, chlorophyll and soil retention. SAL-urea Zn increased shoot biomass, NAC-urea Zn increased Zn grain accumulation by 47%. After the treatment on day 25, SAL-urea Zn increased the chlorophyll content. Soil retention results revealed that NAC-urea showed highest amount of residual Zn which was 2.2mg/kg in soil and residual phosphorus was 14mg/ kg in soil.

METHODOLOGY

3.1 Materials and Methods

The research was divided into three phases. In the first phase of the research Mesoporous Nanosilica particles (MSN) were synthesized and then it was loaded with ZincOxide nanoparticles. Then in the next phase, urea was coated with an inner and an outer coat. In the final phase, water and sand column release tests were performed to evaluate and compare the performance of the synthesized product.

3.2 Phase I of Research

Synthesis of Mesoporous Nanosilica particles (MSN)

For the synthesis of mesoporous silica nanoparticles (MSN), the procedure used was that described by Wanyika et al. (2012). First, 400 mL of deionized (DI) water was measured and then transferred to a clean beaker. To this, 0.9 g of cetyltrimethylammonium bromide (CTAB), a surfactant and pore directing agent was also added. CTAB was dissolved in the mixture through magnetic stirring at room temperature to enhance the homogeneity of the solution.

In the second beaker 100 mL of ethanol was also added as a co-solvent to the solution. To this, we added 6 mL of tetraethyl orthosilicate (TEOS), the silica source slowly. TEOS is one of the most important components in the formation of silica network of MSN. After complete dissolution of the CTAB, the speed of stirring was increased to 700 rpm to form a vortex. To achieve homogeneity in the reaction mixture and to control over the reaction rate, ethanol-TEOS was slowly added to the CTAB solution. This slow addition also avoids the early nucleation of silica particles and enables the development of well-dispersed nanoparticles.

The mixed solution was then let to mix for an extra 4 hours, during which the hydrolysis and condensation of TEOS occurs in the presence of the CTAB micelles. This process led to the synthesis of silica nanoparticles with a well-defined mesoporous structure. The reaction conditions such as stirring rate and time were important in determination of the particle size and pore structure of the MSN in order to achieve high yield and consistent quality of the synthesized material.

After 4 hours, the contents of the beaker were shifted into falcon tubes. The tubes were centrifuged at an rpm of 6000 after which MSN pellets were formed. The solution was decanted leaving the MSN pellet at the bottom. The MSN was then washed thoroughly using DI water and ethanol. In each cycle of washing, DI water/ ethanol was added in the tube and vigorously mixed and then sonicated for 15 to 20 mins after which it was centrifuged again. After washing it thoroughly, the MSN was taken out from the tubes into a China dish and dried in an oven at 70°C for 8 to 10 hours. Upon complete drying the MSN forms clumps which can then be grinded in pestle and mortar to achieve a free-flowing powder. Then the MSN powder was calcined in a muffle furnace at a temperature of 650°C for 6 hours. After calcination MSN was washed again with DI water and ethanol the same way as before and then dried in oven and stored in desiccator.

Synthesis of Zn loaded MSN

Synthesis of MSN@Zn utilized mechanochemical synthesis combined with wet impregnation method (Lihitkar et al., 2012). and The as-synthesized MSN were then used to encapsulate zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2$) to introduce Zn into the mesoporous structure. In loading process, 0.3 g of MSN and 3 g of $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ were taken in a clean mortar for the next procedure. The selection of $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ as a Zn precursor was well considered since its solubility and chemical nature enable it to diffuse well into the mesopores of MSN. The loading process was started by adding 10 mL DI water to the mixture slowly. DI water was added gradually to prevent the dilution of the solution, and it was added to the mixture until it resembled a slurry. At this point the water addition was interrupted, and the slurry was mixed vigorously using a pestle. This manual mixing made the distribution of $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ uniform across the surface of the MSN and penetration into the pores possible. The mechanical action of grinding also increased the contact surface between $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ and the MSN. The final portion of DI water was then added to the slurry and stirred to render the slurry completely homogenized. This two-step process made sure that $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ is well anchored into the MSN structure before proceeding to other steps such as drying or calcination that would fix the loaded Zn into the MSN network.

The mortar was then emptied into a falcon tube. This process was repeated until all the as-synthesized MSN was used. Then the falcon tubes were centrifuged at an rpm of 6000 after which $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ loaded MSN collected at the bottom of the tubes. The

solution was decanted, and the pellet was washed with DI water and ethanol the same way as before, but this time sonication was skipped. Then the synthesized Zn loaded MSN (MSN@Zn) was emptied from the falcon tubes into a China dish and dried at a temperature of 70°C for 8 hours. After drying, the solid mass then grinded using a pestle and mortar and then it was calcined in muffled furnace at 550°C for 5 hours to convert Zn(CH₃CO₂)₂ loaded MSN into ZnO loaded MSN- MSN@ZnO.



Figure 3.1: Zinc loaded MSN (MSN@Zn)

3.3 Phase II of Research

Synthesis of polyols from Cotton Stalks

Employing the method reported by (Olszewski et al., 2021) liquefied cotton stalks were synthesized from cotton stalks. Cotton stalks were procured from Faisalabad.

Cotton stalk polyol blend was prepared as follows: the cotton stalks were dried in an oven at 80°C for 24h to reduce the content of moisture. The dried stalks were also milled into fine powder and passed through 250 µm mesh size. This finely sieved powder was then transferred to a plastic bag to be used later.

In a three-neck flask, the following were added: 12g of concentrated sulfuric acid (H₂SO₄), 40g of glycerol and 360g of PEG-400. The flask was fitted with a reflux assembly consisting of a reflux condenser, a thermometer and hot plate with stirring attachment. After the temperature reached the desired and a constant temperature of 140°C, the sieved cotton stalk powder in the amount of 20 g was gradually added to the mixture while stirring. The reaction mixture was stirred for 90 minutes at 140°C in

order to perform the liquefaction process and convert the cotton stalks into a polyol blend.

After 90 minutes the flask was taken off the heat and allowed to cool to room temperature. The resulting polyol blend was in the form of a highly viscous liquid that was then carefully poured into a glass bottle. This blend can later be used as a biopolyol for polyurethane production, which will be environment friendly rather than the polyols obtained from petroleum products.

Polyurethane Coated Urea

(Ma et al., 2022) reported the dual coating urea. to coat the urea granules with bio-polyurethane, 100 g of urea was placed into the pan coater machine already preheated at 70°C. The granules were tumbled for 10–15 min to allow for uniform heating. After the granules were uniformly heated, a prepared solution of the coating agents was used. This blend consisted of 0.2g liquified cotton stalk, 0.2g PEG-400 and 0.4g siloxane, mixed together with 0.9g MDI. The components were shaken vigorously until the mixture became frothy, so that polyurethane can be well activated. The foamy coating material was then poured over the rotating urea granules, helping the foam to set uniformly to the granules. The rotation of the machine assisted in realizing an even thickness of the layer. The process was repeated several times to develop several layers of the bio-polyurethane coat till the required thickness was achieved. Between each layer and after applying a granule layer, the granules were allowed to set and dry slightly so as to achieve a strong bond. This method guarantees that the granules of the urea are protected by a hard, biodegradable polyurethane layer that allows for a controlled release of nutrients. The process also emphasizes the use of sustainable raw material such as liquified cotton stalks in farming as fertilizer.

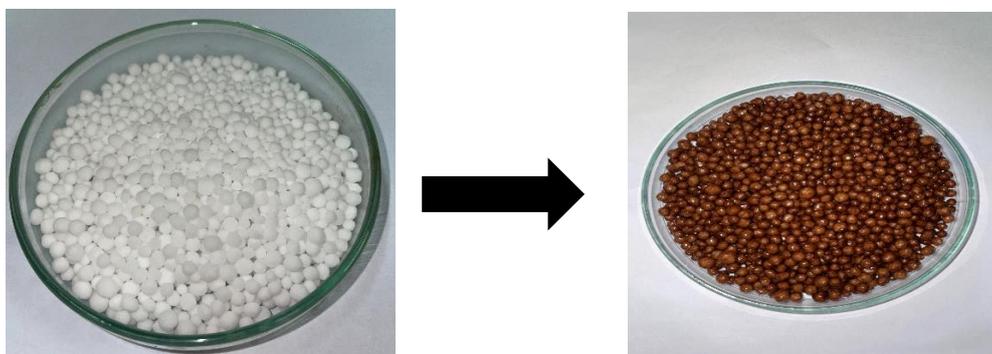


Figure 3.2: Coating Conventional urea with Bio-polyurethane to form BPCU.

Hydrogel Coated Urea

To functionalize BPCU with a dual outer layer of MSN@ZnO embedded in a hydrogel matrix, a procedure was followed as outlined below. First, 10 ml of DI water was taken in a beaker and then 0.4 g of MSN@ZnO was dispersed into the beaker. To a different beaker, 0.6 g of sodium alginate was added and dissolved in 50ml of DI water while stirring until the solution was homogeneous. The content of both beakers was then poured together to form one solution and sonicated for 5 minutes to enable the dispersion of the MSN@ZnO in the alginate solution.

In addition, a copper sulfate (CuSO_4) solution was prepared by directly dissolving CuSO_4 in DI water. The hydrogel matrix was then applied by using the dip-coating method. Small portions of BPCU were placed and carefully coated in the MSN@ZnO and sodium alginate solution. Right after the BPCU granules were coated with sodium alginate solution, they were transferred to the CuSO_4 solution. This caused ionic crosslinking between sodium alginate and Cu^{2+} ions to form stable hydrogel layer around the BPCU. This process of coating and crosslinking was repeated several times in order to obtain the required thickness of the hydrogel layer in order to obtain the dual-coated urea (DCU).

3.4 Phase III of Research

Water release Tests for N and Zn

Water release tests were conducted in accordance with ISO 18644:2016 to assess the efficiency of N and Zn released from the BPCU and DCU, respectively, where uncoated urea was used as control. For each test, 10 g of the respective sample was weighed and put in a nylon bag before being used. These bags were then placed in 250 ml quantities of DI water contained in individual reagent bottles. The bottles were placed in an incubator at room temperature as per the ISO standards. At different time intervals, over a 30-day period, water was transferred from each reagent bottle to be stored in plastic bottles for analysis to be done later. The immersion conditions were kept constant by adding fresh water to the glass bottles after each drainage. Such a systematic collection enabled tracking of N and Zn release profiles in time. The water samples collected were used to estimate the total release rates of nutrients and compare it with the results of uncoated urea.

Sand Column Release Tests for N and Zn

The sand column release test procedure mentioned by (Ozores-Hampton & Carson, 2014) was used to perform this test. Several equipment was used to set up the sand column setup these included PVC pipes fixed on a wooden stand with Buchner funnels placed beneath them. First, the sand was washed with 2% HCl to remove any dirt in the sand then the sand was washed several times with DI water to remove any interferences. After washing, the sand was placed inside the PVC pipes which were 12" long and 2-3" in diameter. The sand was filled in the pipes up to three quarters of its length. Subsequently, 10 g each of BPCU, DCU and uncoated urea were uniformly dispersed on the sand layer in different columns. The rest of the inside of the pipes was then packed with the washed sand. After that, about 200 ml of DI water was carefully poured from the top of each column and the water was let to pass through the sand layer and the leachate was collected in plastic bottles that were placed at the bottom of each column. The leachate collected was preserved to be analysed later in order to establish nutrient release patterns. The process was then carried out systematically at various time intervals up to 30 days in order to separately assess the ability of the samples to release nitrogen and zinc under test conditions.



Figure 3.3: Leachate collection from Sand columns

Total Kjeldahl Nitrogen (TKN)

Method described in ("Method 351.2, Revision 2.0: Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry," 1993) was used with some modifications to carry out Total Kjeldahl Nitrogen (TKN). To determine total nitrogen 10ml of sample

was added into digestion tubes, followed by addition of 0.1 g Copper Sulphate (CuSO_4), 3 g Potassium Sulphate (K_2SO_4) and then a final addition of 20 ml concentrated H_2SO_4 . The digestion of the sample was carried out in DK-6 heating digester (VELP Scientifica, Italy) and the distillation was done in UDK-129 distillation unit (VELP Scientifica, Italy) with 40% NaOH and 4% boric acid solutions. After distillation, 6-7 drops of mixed indicator were added into the distillate collected in the breaker which was then titrated against 1.23N HCL. The consumed amount of HCL was recorded for each titration. Then TKN formula was used to measure 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.

Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) was utilized to quantify Zn release from DCU. The method involved analysing all collected leachate samples from both the water release and sand column experiments. AAS offered high precision in determining Zn concentrations, enabling the evaluation of DCU's performance in controlling Zn release. This data was critical for assessing the coating's ability to provide a controlled and sustained nutrient supply over the experimental period.

RESULTS AND DISCUSSIONS

4.1 Characterization Analysis for MSN and MSN@ZnO

1) Fourier Infrared Spectroscopy (FTIR)

The FTIR spectra shows characteristic peaks of silica particles. The peak around 3500cm^{-1} can be attributed to stretching vibrations of hydroxyl groups and the peak at 1632cm^{-1} are of OH bending vibrations, which both are characteristic of SiO_2 molecules (Su et al., 2021), shown in figure 4.1. The vibrations that emerged around 1087cm^{-1} and 804cm^{-1} are asymmetric and symmetric vibrations of Si-O-Si respectively. After the incorporation of ZnO the OH tensile and flexural vibrations still showed up but there is a decreased intensity in transmittance which could be a result of coordination between the lone pair of electrons present on oxygen atoms and ZnO (Jiang et al., 2024).

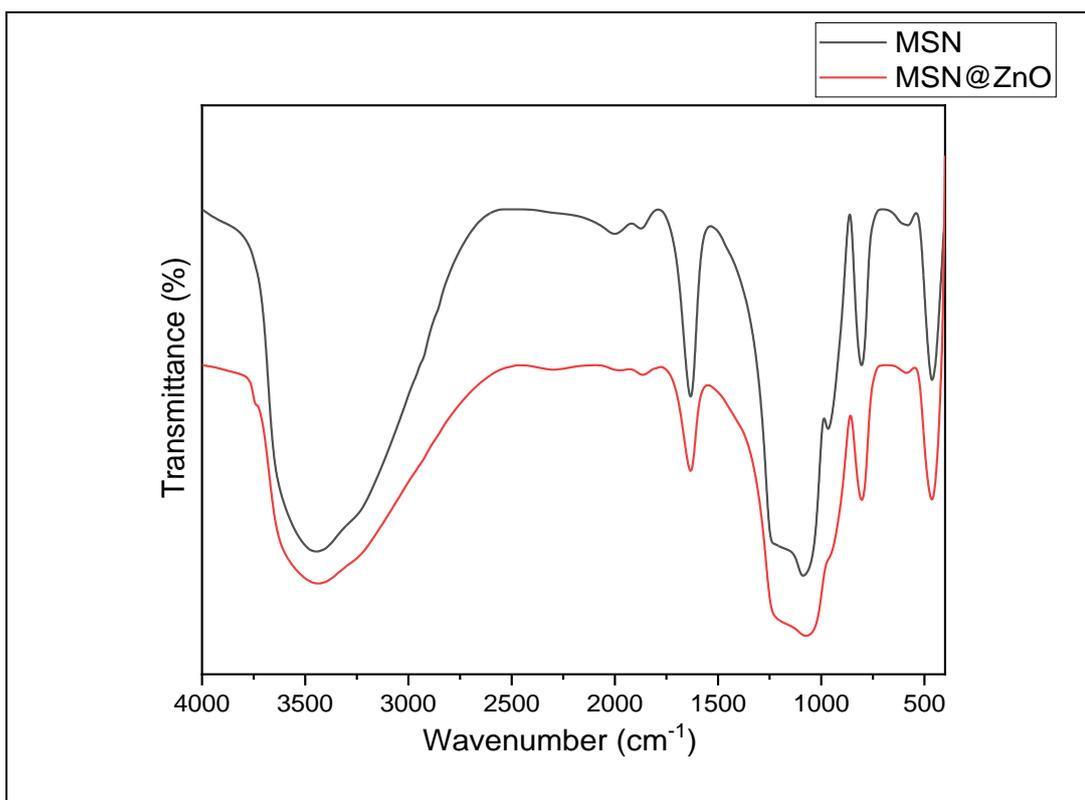


Figure 4.1: FT-IR spectra of MSN and MSN@ZnO. This FTIR graph compares the spectra of MSN (black curve) and MSN@Zn (red curve). The spectrum of MSN shows characteristic peaks around 1100 cm^{-1} and 1600 cm^{-1} , which are typical for silica, while the spectrum for MSN@ZnO shows additional peaks that likely correspond to the Zn-

O stretch, indicating the successful incorporation of ZnO into the MSN. The shift in the peaks and the appearance of new ones in the red curve suggest changes in the chemical environment after ZnO loading.

The peak at 966cm^{-1} is attributed to tensile vibration of Si-OH, but after loading ZnO in MSN the peak disappears (Majidi et al., 2024) which indicates successful incorporation of ZnO in MSN as the disappearance of the peak indicates that all Si-OH groups have interacted with ZnO (Wen et al., 2019). ZnO shows a characteristic peak of Zn-O stretching vibrations at around 460cm^{-1} but SiO_2 molecules also a peak around this value corresponding to the bending vibrations of Si-O-Si because of which a masking effect could take place causing combining or interference among the two. So, the peaks shown in Fig.4.1 around this range can be attributed to the interaction of both of these functional groups (Li et al., 2008).

Table 4.1: Characteristic peaks of functional groups of FTIR analysis of MSN and MSN@Zn are shown. The two samples show hydroxyl groups indicated by OH stretching at around $3447\text{--}3436\text{ cm}^{-1}$. The MSN@Zn also has a peak at 464 cm^{-1} for Zn-O bonds and the other peaks are associated with the silica framework.

MSN	ZnO loaded with MSN	Functional Groups
3447	3436	OH stretch
1632	1632	Bending vibrations of adsorbed water
1087	1073	Asymmetric Si-O-Si
966	Absent	Si-OH
804	803	Symmetric Si-O-Si stretch
463	464	-Bending vibration of Si-O-Si -Combination of stretching modes of Zn-O and the bend vibration of Si-O-Si

2) X-ray Diffraction (XRD)

The amorphous nature of MSN and MSN@ZnO was studied by Wide angle XRD. Figure 4.2 shows that both MSN and the nanocomposite displayed a peak between 20 to 30° which confirms the amorphous nature of the silica particles (Prasanna et al., 2020). The peak between 20 to 30° changes shifts very slightly for the nanocomposite from 22° to 23° and the intensity of the peak also gets reduced as ZnO gets incorporated in the MSN. The XRD of MSN@ZnO shows no additional peak. Han et al. (2022) reported no other additional crystal peaks showed up for the nanocomposite indicating that nano-ZnO was present in amorphous form.

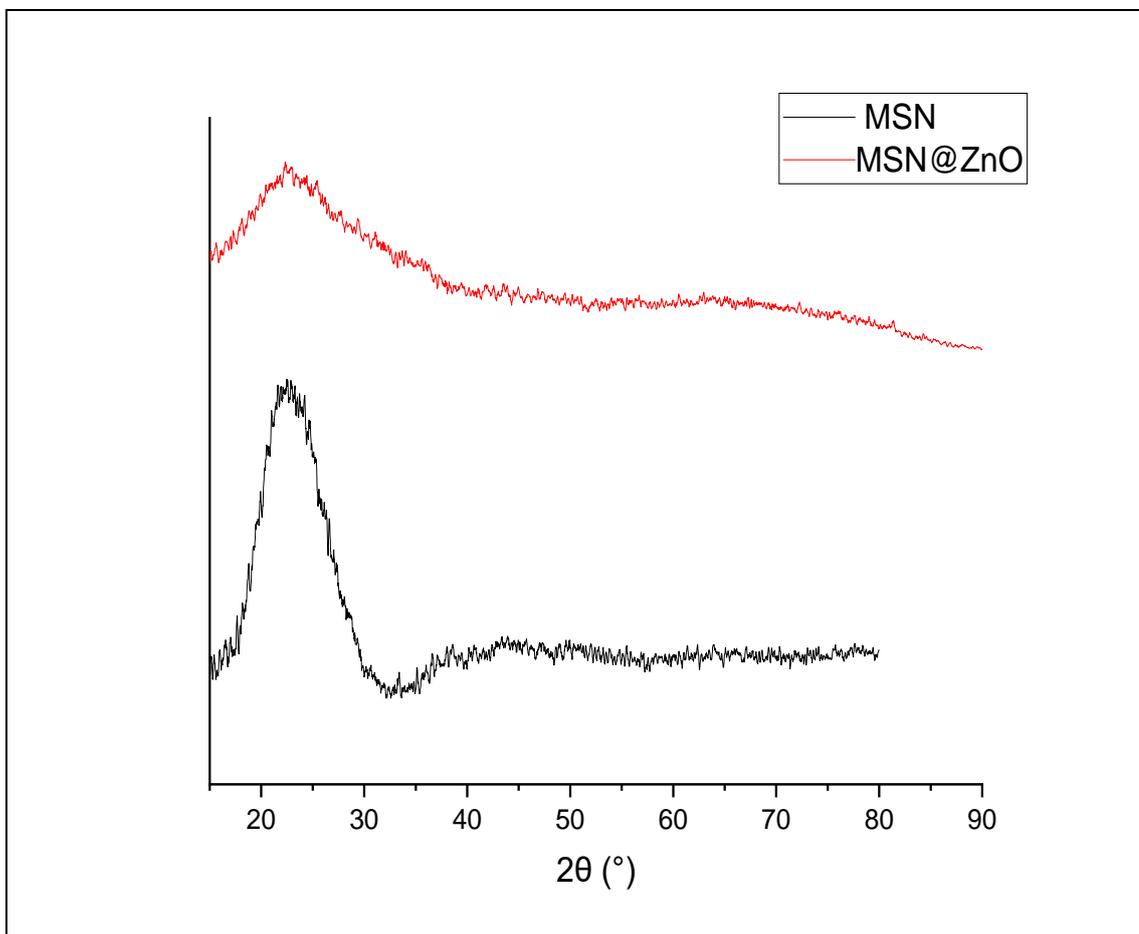


Figure 4.2: This is the X-ray diffraction (XRD) graph of the patterns of pure MSN (black line) and those of MSN@Zn (red line). The wide peak centered around 22° is characteristic of the silica. Absence of ZnO peaks indicates the presence of amorphous ZnO particles.

3) Brauner-Emmett-Teller (BET)

- **Adsorption Isotherm**

Type IV adsorption isotherms of MSN and MSN@ZnO displays the mesoporous structure of both composites and the impact of ZnO loading on the adsorption capacity of MSN. Figure 4.3 shows that across increasing relative pressures both MSN and MSN@ZnO adsorb gas at the same rate.

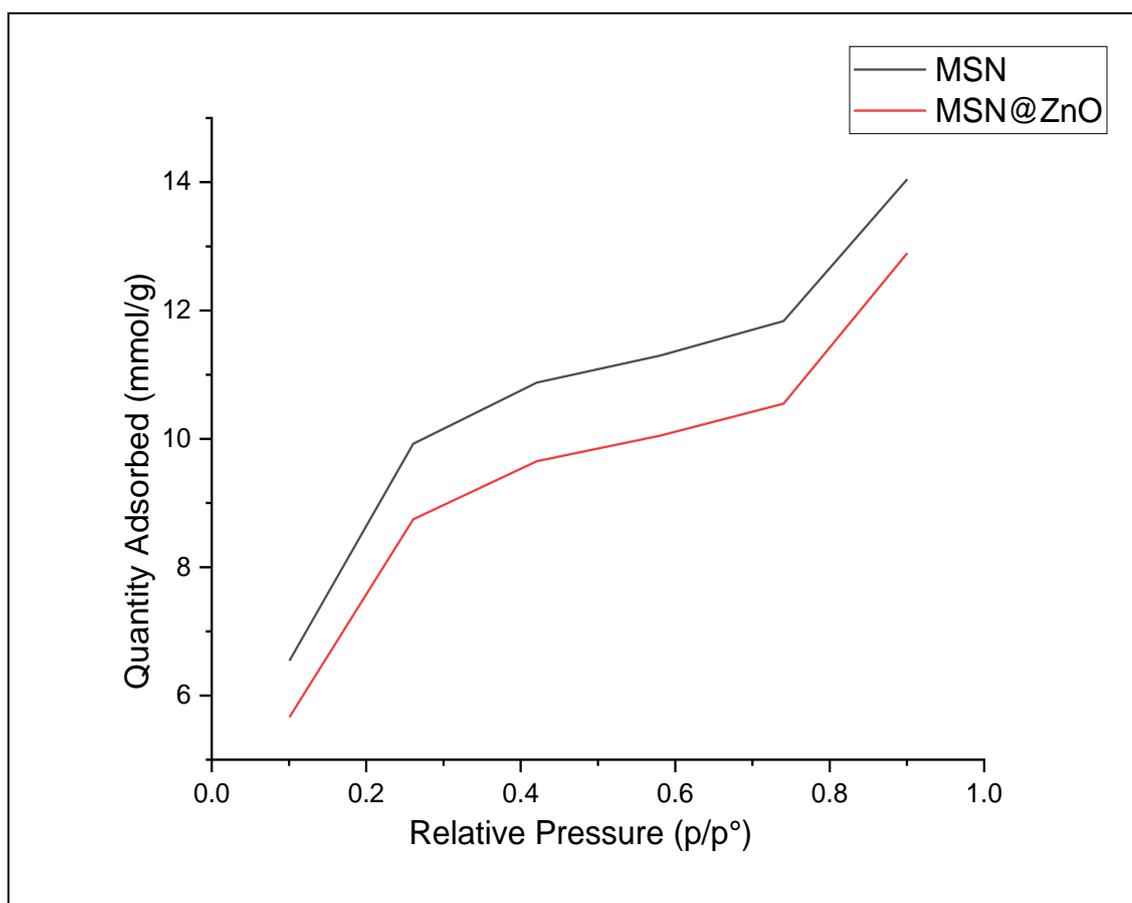


Figure 4.3: Adsorption Isotherm of MSN and MSN@Zn. This graph depicts the nitrogen adsorption-desorption isotherms of MSN and MSN@ZnO, showing the relationship between the quantity adsorbed and relative pressure. MSN exhibits higher adsorption capacity compared to MSN@ZnO, indicating a reduction in pore accessibility or volume after ZnO loading.

Following are the various phases displayed by type IV adsorption isotherm reported by (Hwang & R. Barron, 2011).

i) Low Relative Pressures

At lower pressures the quantity of the gas adsorbed is rapid due to the availability of high energy adsorption site. The rapid adsorption at lower relative pressures indicates the formation of monolayer due to the strong interactions between the nitrogen gas and the surface of the MSN and MSN@ZnO.

ii) Intermediate Relative pressure

At intermediate relative pressures a plateau occurs indicating that the rate of adsorption of the gas on these pressures have slowed down. This is characteristic of the capillary condensation occurring within the mesopores.

iii) Higher Relative Pressure

It shows the formation of monolayer at low pressures is followed by the formation of multilayers at higher relative pressures as the isotherm again shows a steep rise in the quantity of the gas adsorbed.

Although the rate of gas adsorbed is same for MSN and MSN@ZnO, but the amount of gas being adsorbed at varying relative pressures is less for MSN@ZnO. This is due to the incorporation/ blockage in the pores of the MSN by ZnO which causes a reduction in the surface area of the MSN. So, when the surface area is reduced the gas adsorbed is also reduced.

- **Pore size Distribution**

Pore size distribution curve of MSN and MSN@ZnO shows the relation of pore width with pore volume for both the composites. This pore size distribution graph reveals that most of the pore diameter for both MSN and MSN@ZnO lies between the range of 20Å to 30Å as shown in figure 4.4. Generally, the graph also shows that as the pore volume decreases, the pore width increases. The trend is similar to the results reported by Shen et al. (2018). This indicates that a pore volume of 2.1 cm³/g·Å at a pore width of 20Å for MSN but when Zn is loaded in MSN the pore volume shrinks to 1.7 cm³/g·Å with little to no difference in pore width. The decrease in volume after the addition of Zn indicates that Zn has successfully lodged inside the pores which has caused a decrease in pore volume.

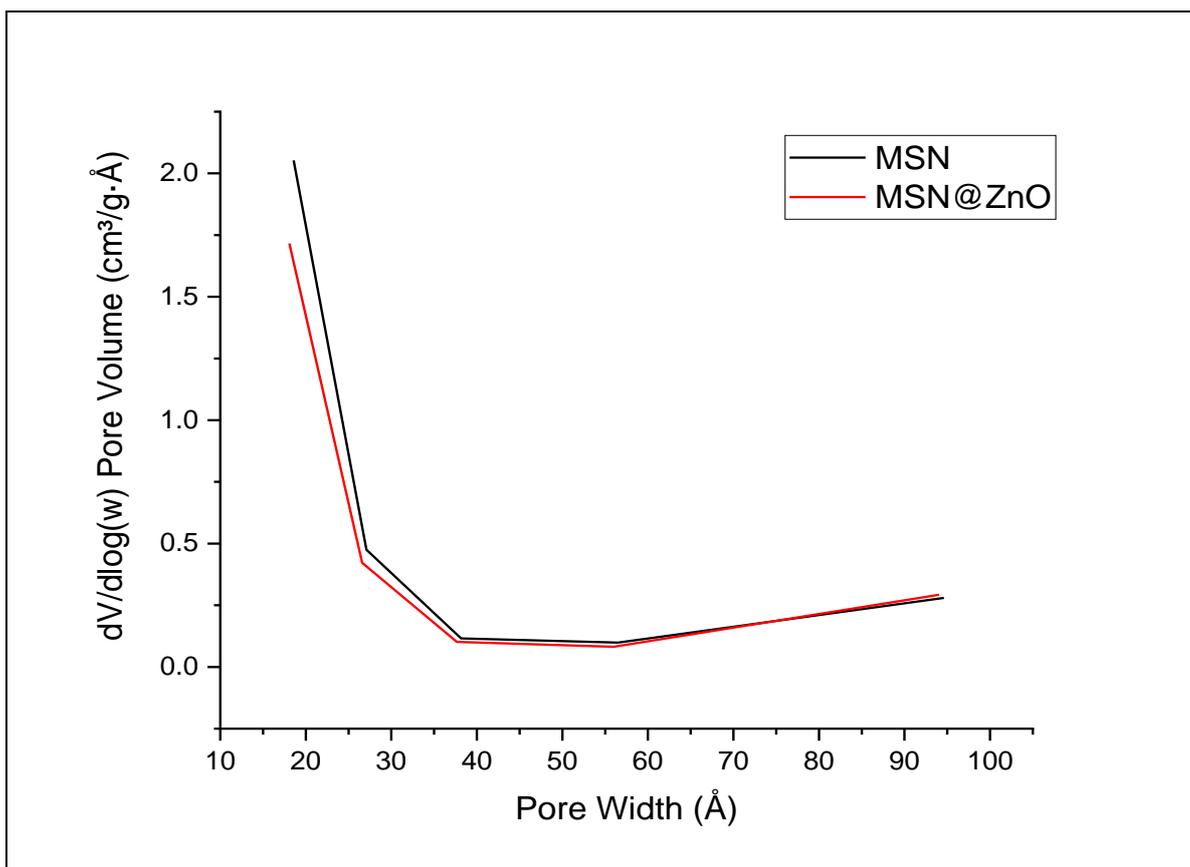


Figure 4.4: The pore size distribution of MSN and MSN@ZnO particle is presented in this graph. The sharp peak at smaller pore widths which are around 20–30 \AA is indicative of the mesoporous nature of both samples, with MSN showing a relatively higher pore volume compared to MSN@ZnO. The reduction in pore volume for MSN@ZnO indicates a successful loading of ZnO within the mesopores, partially blocking them.

4) Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectrum (EDX)

SEM images of MSN formed in clusters and the images show a size of an individual particle within nanometer range which is around 70nm. They also show a spherical morphology of the nanostructures.

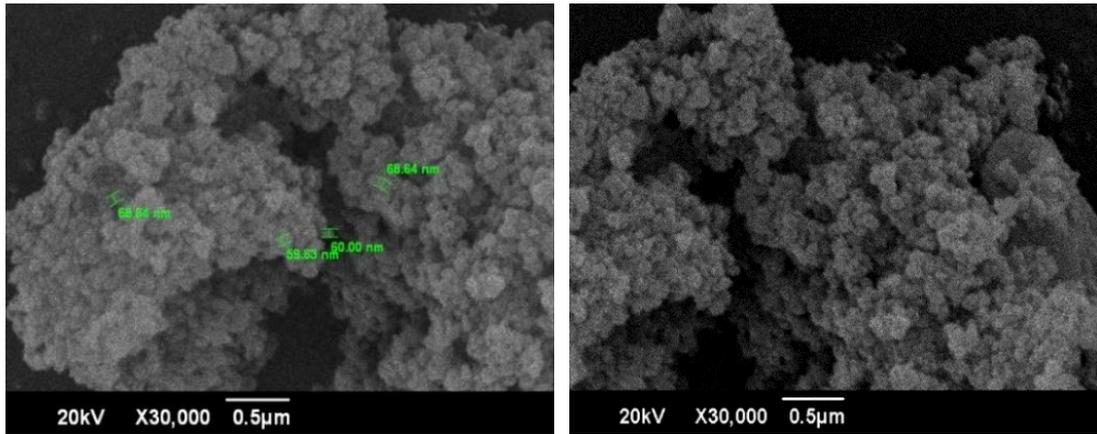


Figure 4.5: SEM images of MSN. The images show clusters of MSN with a spherical morphology. The image also highlights the size range of the nanoparticles formed which is in range of 50nm to 70nm.

The following data, figure 4.6 and table 4.2 show elemental composition of MSN@ZnO.

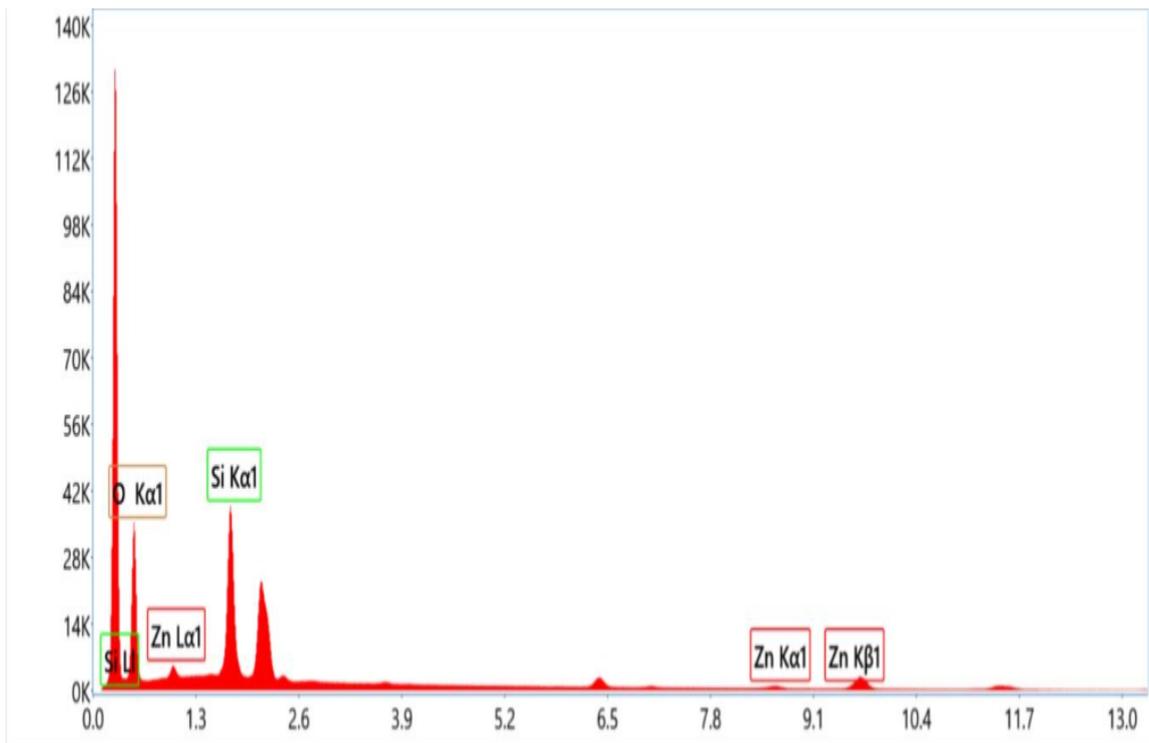


Figure 4.6: Energy Dispersive X-ray spectrum. The Energy Dispersive X-ray (EDX) spectrum shows characteristic peaks for the elements present in the MSN@Zn sample. Peaks corresponding to silicon (Si K α 1), oxygen (O K α 1), and zinc (Zn L α 1, Zn K α 1, Zn K β 1) are visible.

Table 4.2: Elemental composition, weight % and Atomic % of MSN@Zn. The amounts of the elements present in the MSN@Zn sample are quantitatively shown in the table above. The major elemental composition of the sample is as follows; Oxygen was the most abundant with a weight percentage of 62.1% followed by silicon at 31.9% and Zn at 6.0%.

Element	Weight %	MDL	Atomic %
O K	62.1	0.19	76.0
Si K	31.9	0.10	22.2
Zn K	6.0	0.54	1.8

4.2 Characterization Analysis of Cotton Stalk Derived Polyols

1) Gas Chromatography Mass Spectrometry (GC-MS)

The GCMS results of polyols synthesized from cotton stalks show that a large quantity of polyhydroxy compounds were synthesized which are needed for a successful synthesis of bio-polyurethane (Kyei et al., 2022). The following table, lists the polyhydroxy compounds found in cotton stalk derived polyols:

Table 4.3: GCMS report of Polyhydroxy compounds in the polyols synthesized from cotton stalks.

Sr No.	Compound Name
1	Propanoic acid
2	2-[2-(Tert.butyl-dimethyl-siloxy-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-1-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	Protoadamediol
14	Dibromophloretic acid
15	5-Methylthiazoline-2-resocinol
16	1,2-Dideoxy-1-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-1-erythro-pentitol
30	d-Altronic acid
31	1,3-Methylene-d-arabito
32	2-Hydroxy-2-methylbutyric acid
33	2-exo-5-endo-Protoadamediol
34	5-tridecafluorohexyl
35	1,2-Propanediol
36	Uridine
37	1,3-Cyclohexanediol
38	Monomethylene-1-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,

4.3 Characterization Analysis of Bio-polyurethane Layer

1) Fourier Informer Infrared Spectroscopy (FTIR)

The FTIR spectra confirmed the successful synthesis of bio-polyurethane for coating of urea. Figure 4.7 displays that the peak around 3290cm^{-1} is of N-H stretch and that at around 1530cm^{-1} is of N-H bend, these peaks are characteristic to polyurethane (Arévalo-Alquichire et al., 2020).

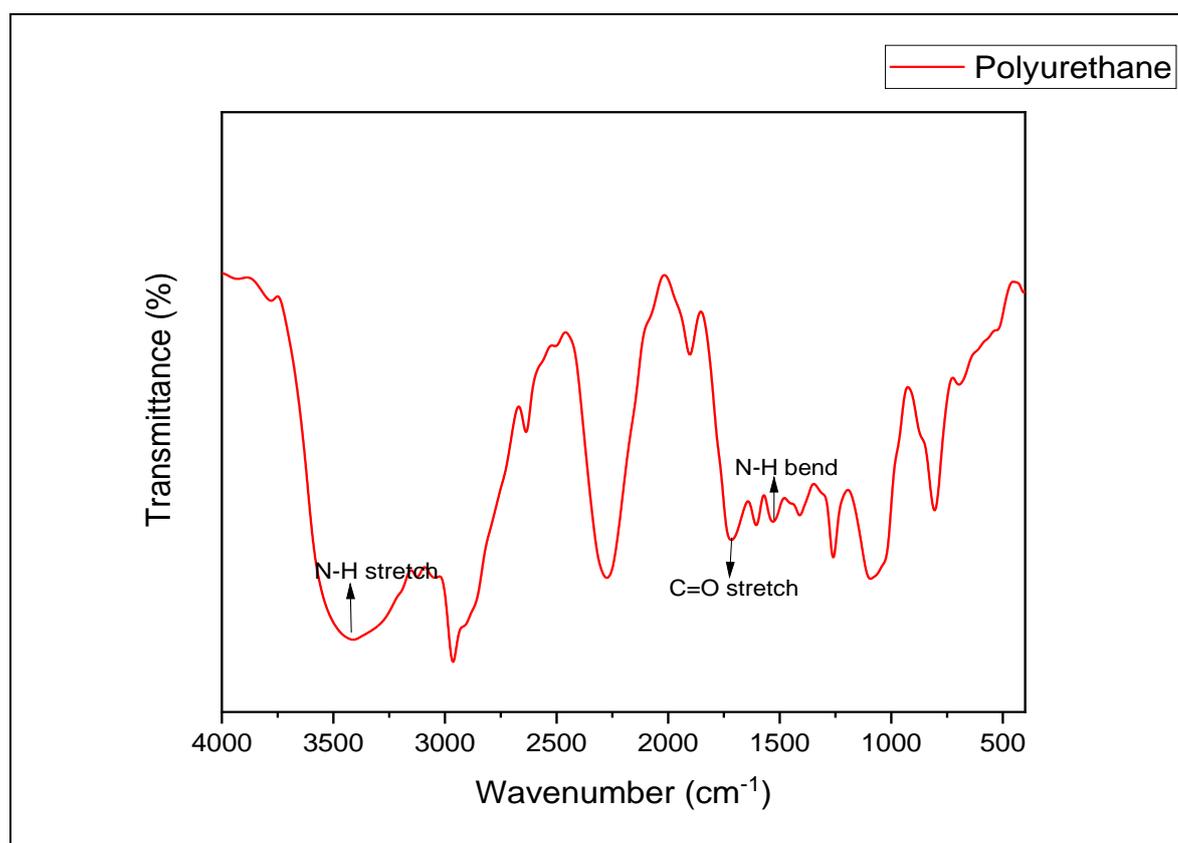


Figure 4.7: FTIR spectra of Bio-polyurethane. The figure highlights various characteristic peaks of a polyurethane material which are N-H stretch, C=O stretch and N-H bend.

The peak at 1730cm^{-1} can be attributed to stretching vibrations of carbonyl groups formed from the saturated chain, from the cyclic ketone groups or aldehyde which links to the acetyl groups that are present in hemicellulose and/ or cellulose present in the agricultural waste, which is cotton stalks in this case. Also, the peak around 2960cm^{-1} can be attributed to C-H stretching present due to the methylene or methyl groups in cellulose of cotton stalks (Ji et al., 2014). The two peaks that emerge at around 1260cm^{-1} and 1900cm^{-1} can be attributed to stretching vibration of C-O-C the presence of these groups can be due to the solvents used in liquefaction process of cotton stalks or due to the products formed when cotton stalks were degraded in the process (Zhang et al., 2019).

2) Scanning Electron Microscopy (SEM)

The SEM images show urea granule with Bio-polyurethane layer coated on it.

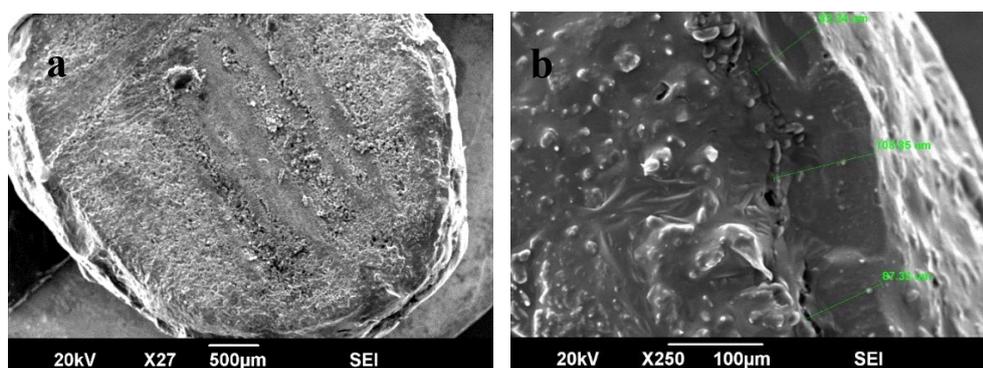


Figure 4.8: SEM image of cross-section of BPCU. The images are taken at two different magnifications. a) A cross-section of a whole urea granule with bio-polyurethane layer surrounding it. b) A close-up image of BPCU, showing thickness of bio-polyurethane layer across various points.

4.4 Water and Sand Column Release Tests for N

1) Water Release Tests

Release profiles of urea which was used as a control, BPCU and DCU were tested in water. The release profiles displayed the typical phases for CRU. The graph in figure 4.9 clearly shows the rapid release of N from conventional urea where all of it was released within 24 hours of being placed in the water. Conventional urea released all of its N in 24 hrs. Whereas, BPCU and DCU shows a steady release profile indicating that

the bio-polyurethane layer has successfully formed a coating around the urea granule. The release pattern is similar to the one reported by Chen et al. (2020).

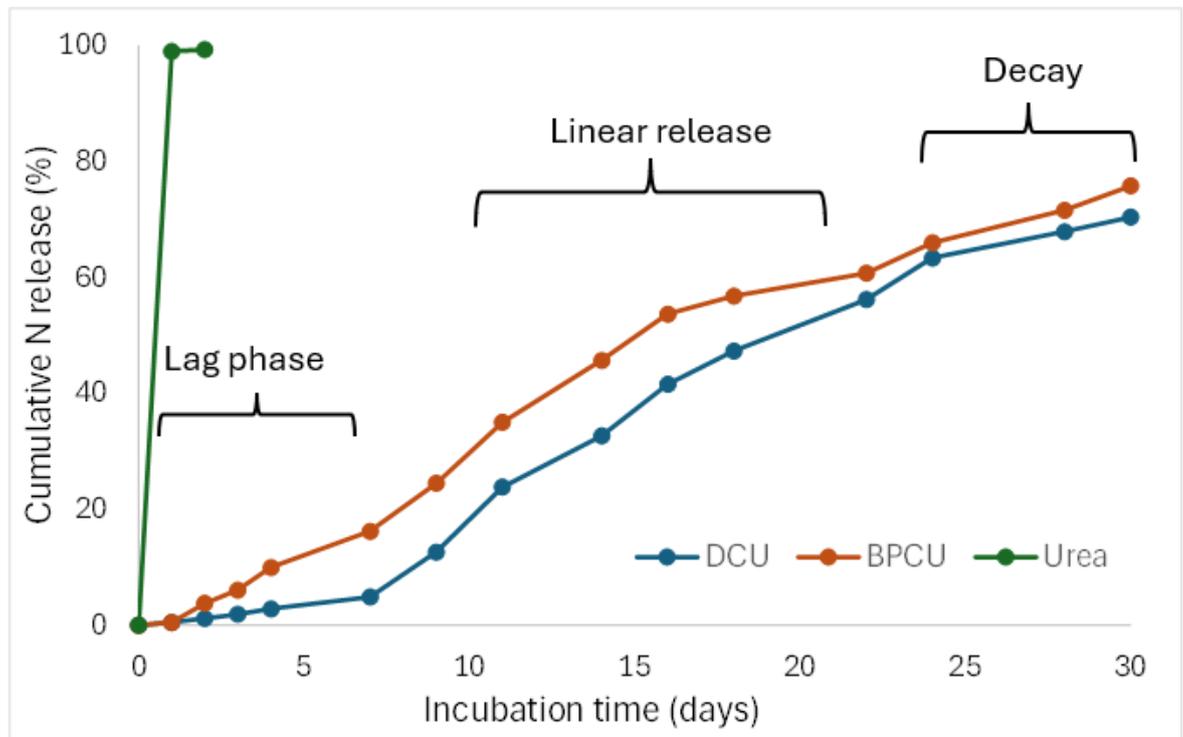


Figure 4.9: N cumulative release rates of Urea, BPCU and DCU in water. The graph shows three phases, namely lag phase, linear phase and Decay phase. The release of N in lag phase is slow while in linear phase the N release shows a steady profile till day 25.

In the initial phase, from day 1 to day 7 a lag phase is observed where it shows a release of 17% and 5% for BPCU and DCU respectively. The small release of N indicates that bio-polyurethane layer remained intact for a time period. Then after day 7 onwards till day 17 a linear phase was observed in which BPCU released almost 60% of N and DCU released 50% of N content. This indicates that in this time period the water gradually seeped inside the layer, dissolving the urea granule and building up an osmotic pressure. Due to which the solution started to diffuse through the barrier. As most of the urea has been spent so in the last phase, little to no N is released. The graph shows that across the whole-time frame, DCU always gave lesser N release as compared to BPCU. This shows that the dual coated urea with a hydrogel layer played a crucial role in delaying the release further as reported by Ma et al. (2022b).

According to (ISO, 2016) the cumulative release mass fraction of the nutrient should be less than 75% in 28 days and the developed products, BPCU gave a release of 71% on day 28 and DCU gave a release of 68% on day 28.

2) Sand Column Release Tests

Sand column release tests gave a similar result as water release tests. The figure 4.10 shows that urea again gave a rapid release of N as for BPCU and DCU a lag release was observed followed by a linear phase then plateauing into the decay phase.

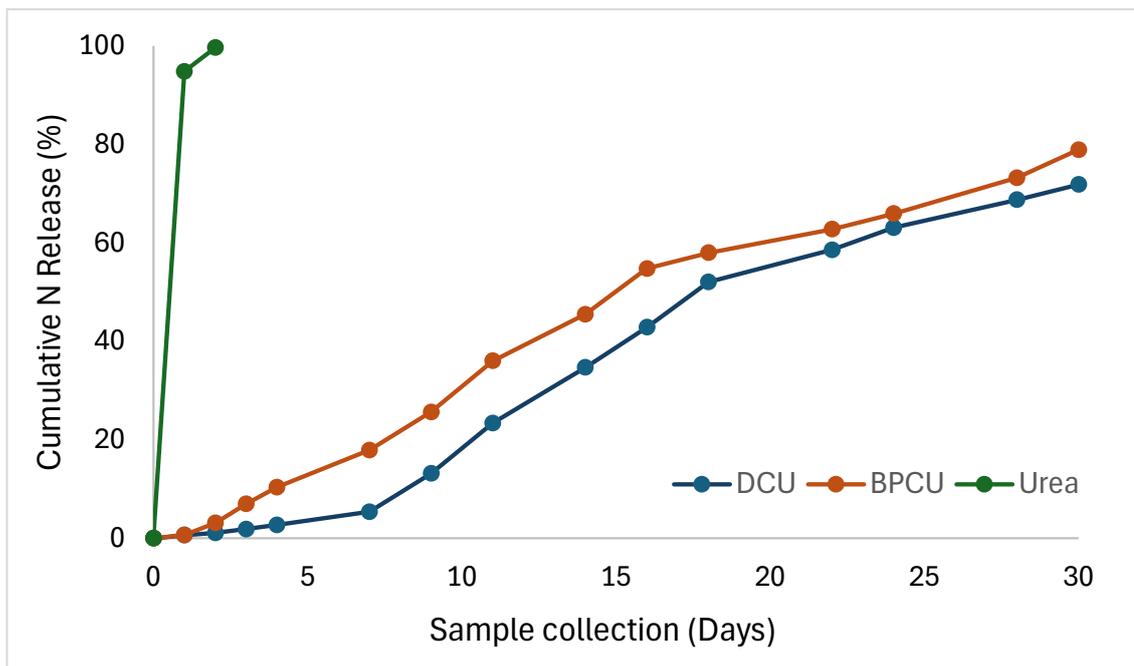


Figure 4.10: N cumulative release rates of Urea, BPCU and DCU in sand columns. The N release is slower in the beginning till day 7. Day 7 onwards the release becomes linear and after day 25 almost all N is released as the graphs slows down again.

The results again indicated that BPCU and DCU delayed the release of N as compared to urea and DCU was much efficient in delaying the release as compared to BPCU in sand as well. BPCU gave a release of 17% and DCU released only 5% of N in 7 days. Then the linear phase extended from day 8 till day 18, at the end of which BPCU and DCU released 57% and 52% of N respectively. The results are indicative of successful bio-polyurethane coat as the release of BPCU and DCU in both medias gave almost the same result, implying that the coating layer is not affected by the environment rather the intrinsic properties of it are at play when put to test.

4.5 Water and Sand Column Release Tests for Zn

1) Water Release Tests

Release pattern of Zn was tested from DCU in water. The figure 4.11 represents the cumulative release of Zn over a span of days, with the y-axis showing the percentage of Zn released and the x-axis denoting sample collection times in days.

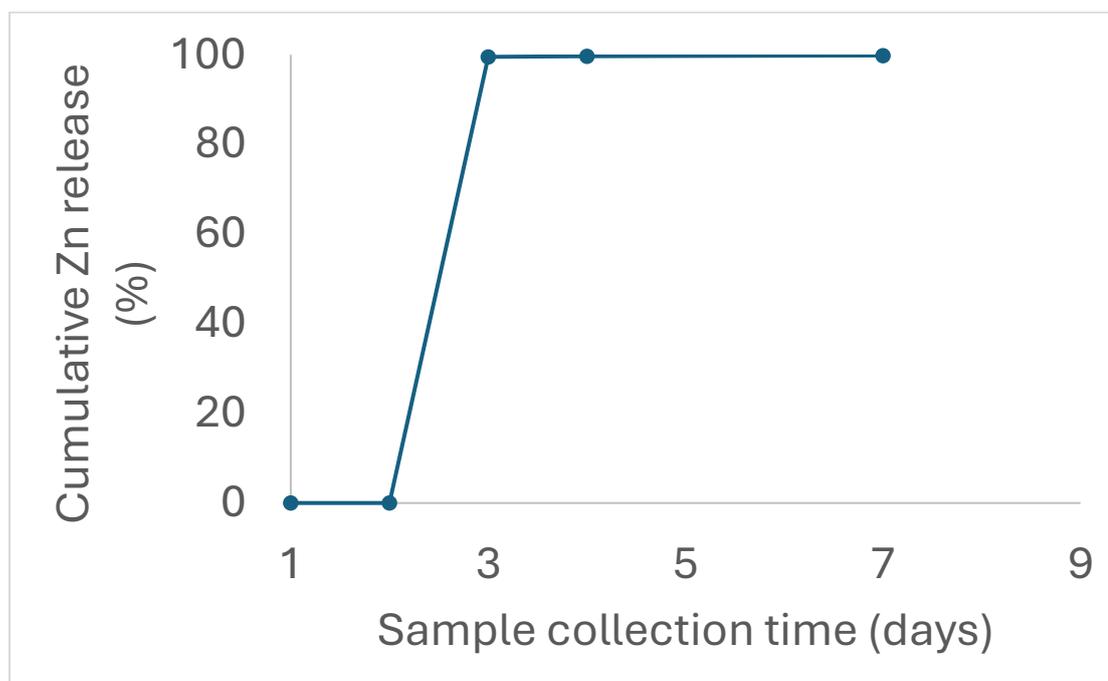


Figure 4.11: Zn release rate from DCU in water. The graph shows that no Zn was released on day 1. On day 2 there was a sudden release of Zn and all of the Zn was released within 24hrs.

Initial Phase (Days 1-2):

Minimal or negligible Zn release is observed in the initial period, suggesting that the coating or matrix effectively delayed the release, preventing immediate leaching of Zn. This phase represents the controlled-release mechanism at work.

Rapid Release Phase (Day 3):

By day 3, nearly 100% of the Zn has been released. This sharp increase indicates that the barrier provided by the hydrogel or coating degraded or dissolved under experimental conditions, allowing the release of embedded Zn. This stage might correspond to the complete exposure of MSN@Zn.

Plateau Phase (Days 3-7):

After day 3, the curve reaches a plateau, indicating no further Zn release. This plateau signifies that all available Zn has been leached out and is no longer retained in the matrix or granules.

2) Sand Column Release Test

Zn release profile was also tested in sand columns. The graph shown in figure 4.12 represents the release of Zn in terms of percentage over time. The graph on the left indicates the sample collection time in days on the x-axis and the cumulative Zn release percentage on the y-axis.

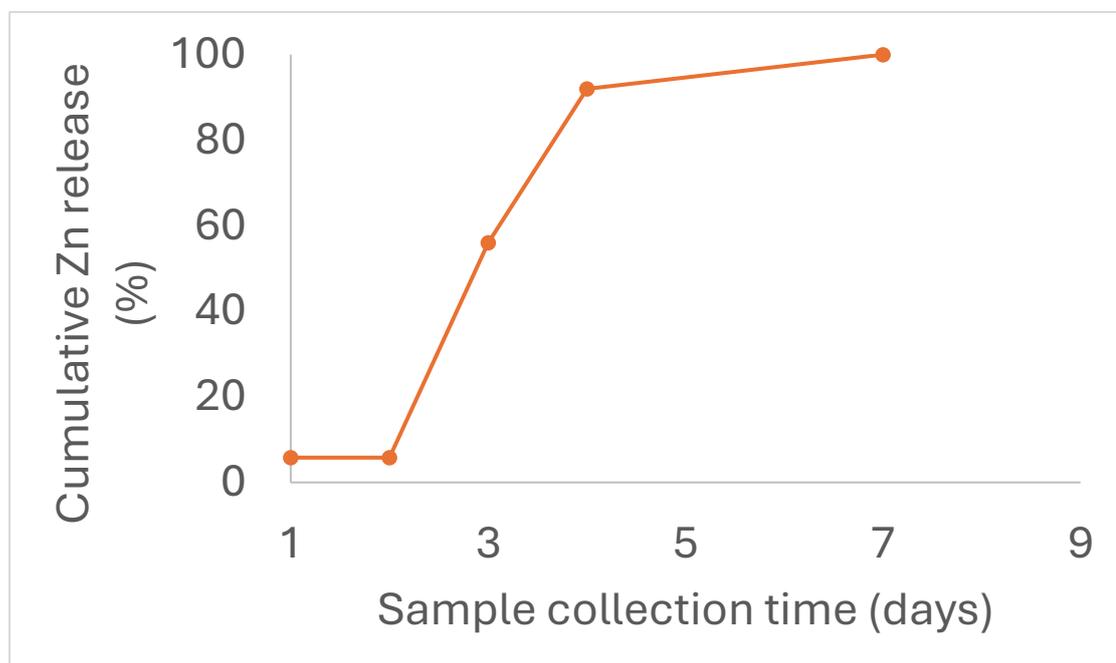


Figure 4.12: Zn release rate from DCU in leachate from Sand column. The graph shows that a little amount of Zn was released on day 1. Then there was sudden release of Zn on day 2 and the release sustained till day 4. Then the graph plateaued off gradually till day 7.

Key observations that were derived from the release pattern were as follows:

Initial Phase (Day 1): In the first two days, there is almost no or very little Zn release, which shows that the coating successfully confines the Zn at the beginning.

Rapid Release Phase (Day 3): A sharp increase takes place, and it releases 60–70% of Zn. This, therefore, represents the point at which the coating is compromised and Zn that was entrained in the coating begins to be released.

Stabilization (Day 7): As it can be seen on day 7 almost 100% of Zn is released, this might be due to dissolution or diffusion of Zn from the coated material. Umar et al. (2022) also reported a somewhat similar Zn release pattern from their product that showcased an initial sudden release of Zn followed by a gradual release over a time period.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The research aimed at developing and testing out the release of CRU, synthesized using a bio-polyurethane layer as the first coat (BPCU) and a second coat of hydrogel layer embedded with Zn loaded MSN (DCU). The goal of this study was to address environmental challenges created as a result of nitrogen wastage from urea fertilizers.

The results from this study indicate successful synthesis of dual-coated controlled release urea. The bio-polyurethane layer was formulated, using cotton stalks and the hydrogel layer having Zn micronutrient in it delayed the N release and gave a Zn supply as well which could be a step towards introducing sustainable agriculture in Pakistan.

The CRU formulated was tested in water and sand columns. The release in both media showed a similar pattern with a lag phase followed by a linear release phase and a decay phase. Where, DCU delayed the N release far better than BPCU. The release of N was in line with ISO 18644:2016 with BPCU showing a release of 71% on day 28 and DCU giving a release of 68% on day 28.

The Zn release pattern of DCU in water and sand column was also tested. In water, the Zn pattern showed a burst effect where 100% of it was released on day 3, but in sand the release of Zn was much slower. The Zn release extended up to 7 days.

Coating conventional urea fertilizer with bio-polyurethane and Zn embedded hydrogel layer can be a turning point in the agriculture of Pakistan where N losses and Zn deficiency is a pressing concern. Using the developed product can delay the N release which will be beneficial for the environment in various aspects. Also, the Zn delivery system embedded in the CRU will not only enrich the soils with an essential micronutrient but will also be a means of correcting Zn deficiency in the population of Pakistan as well.

5.2 Recommendations

Recommendations made after the completion of the study are as follows:

-It is essential to carry out pot tests followed by field trials in order to study and evaluate the behaviour of the developed products in the real-world environment.

-Biodegradability of the product must be studied to assess the accumulation of the coating material in soil.

-Various other micronutrients that are deficient in various other soils can be incorporated in MSN and their release pattern and effect must be studied.

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