Introduction

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Introduction Chapter 1

1.1. Background of the study

In the next thirty years, the population of the world is expected to reach approximately 1×10^{10} [1]. Most of the food supply will come from agricultural items. Notwithstanding political systems and socioeconomic circumstances, obtaining food security is desirable[2]. In the developing world, where food security is often threatened by population growth coupled with more intense natural disasters like floods, droughts, excessive temperature variability, or rainfall, it is of utmost importance [3]. Furthermore, rising food prices along with economic inequality may negatively affect low-income households' access to and availability of food because of rising food demand and declining agricultural productivity. Hunger and malnutrition are believed to be primarily caused by poverty, war and conflict, natural disasters, climate change, and population growth [4,5]. In the Asia Pacific region, ending hunger and malnutrition is still a top goal despite considerable progress. An estimated 479 million people in the region were undernourished in 2018, making up 58% of the global total [6]. Underutilized and neglected species have great health benefits. For instance, lentils are a good source of micronutrients and can provide enough iron (Fe), zinc (Zn), and selenium (Se) in the diet [7]. In India, the anemia rate is lower in areas that cultivate lentils than in areas that don't. The Indian government adopted food-based strategies to achieve sufficient dietary iron intake, acknowledging the role of dietary diversity in avoiding nutritional anemia. These approaches encouraged the consumption of foods high in micronutrients like vitamin-C-rich fruits, dark-coloured leafy vegetables, and lentils, which are readily available but insufficiently utilized by the deficient in nutrients group[8]. The chickpea, or *Cicer arietinum* L., is a staple grain bean that is widely used worldwide but is most prevalent in the Middle East, northern Africa, and southern Asia. It offers high-quality biological protein. One of the first grain legumes to be domesticated in the ancient world was *Cicer arietinum* L. [9].

The soil is the most significant basic natural resource that determines the long-term viability of any agricultural system. Understanding the soil's morphology, physical properties, and chemical composition provides valuable insights into its dynamics. The Northeastern Region (NER) of India has complicated geological and geomorphic formations with significant rainfall, resulting in diverse soil types and landforms. The Brahmaputra valley is mostly made up of alluvial soils that originated on recent river deposits known as "new alluvium". Inside the valley, a few isolated pockets of pleistocene deposits known as "old alluvium" can be discovered along the foothills and in Bangladesh[10]. Assam is largely an agriculture-dependent state. More than 65% of its total land is agricultural.

A cropping system involves growing crops in a precise order to maximize the use of available resources on farmed land. An effective cropping system aims to maximize production and economic rewards. According to Gangwar et al. [13], having a variable cropping system allows for both economic and environmental benefits. To overcome micronutrient shortages, Indian farmers use a variety of fertilization tactics, including soil application, foliar application, seed treatment, and micronutrient-enriched fertilizers. Micronutrient fertilizers are frequently treated with zinc sulphate, ferrous sulphate, manganese sulphate, and copper sulphate, especially in locations that are weak in these elements. To increase soil health and fertility, Integrated Nutrient Management (INM) practices are recommended, which incorporate the use of chemical fertilizers, organic amendments, and micronutrient supplementation.

Like other critical minerals, Zinc (Zn) is an essential component for crop productivity[15]. Plant metabolism, including the development of cell walls, respiration, photosynthesis, production of chlorophyll, activity of enzymes, and other biochemical reactions, depends on zinc. Agricultural soils vary widely in their zinc concentration and capacity to supply zinc for the best crop growth[16]. There is evidence of a zinc deficiency in soil across the world [17], but notably in India[18–20]. Takkar[21] estimated that 34% of the soils in Assam lacked zinc. Brahmaputra lowlands, which are a component of the Indo-Gangetic plains, were historically used for rice cultivation, so 0.6 mg Zn kg^{-1} is regarded as a critical limit. Micronutrients known as transition metals, such as iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn), are essential for the growth of plants. They are involved in several metabolic functions, including respiration, photosynthesis, and enzyme activation. For instance, iron is a part of the enzyme catalase, which scavenges harmful reactive oxygen species (ROS) to shield plants from oxidative stress. Copper is required for the action of enzymes involved in lignin production, which aids plant structural stability. Transition metals like magnesium (Mg) and manganese (Mn) are essential components of the chlorophyll molecule, which captures light energy during photosynthesis. Without these metals, plants would not be able to efficiently convert sunlight into chemical energy. Traditional fertilizers, such as chemical fertilizers and organic amendments, have long been used in agriculture to improve soil fertility and crop productivity. However, excessive, and incorrect use of these fertilizers can result in nutritional imbalances, soil degradation, and environmental pollution.

The use of nanotechnology in Assamese modern agriculture systems has not been thoroughly documented, but an experiment was carried out in Rabi, 2021–22 at the experimental plot of the Department of Agronomy, Biswanath College of Agriculture (BNCA), Assam Agricultural University (AAU), Biswanath Chariali, Assam, with geographic coordinates of 26°43'30" N and 93°08'08" E, to evaluate nitrogen management in sunflower (*Helianthus annuus* L.) in rainfed farming settings using conventional and nano urea. It was reported that nitrogen management techniques did not significantly affect seedling emergence percentage[26]. Another study worth considering is the "Synthesis, Characterization, and Release of Nano-Enabled Phosphorus Fertilizer in Acid Soils of Assam" which was conducted in 2019-21[27].

On the other hand, if nanofertilizers are generated from natural sources and may comprise bio-based components such as plant extracts, microbial biomass, or bio-waste products, which are synthesized into nanoparticles using environmentally benign procedures. Green nanofertilizers have various advantages, including less environmental impact, biocompatibility, and the possibility for increased nutrient bioavailability and plant growth stimulation. According to Wuana and Okieimen [28], plant tissues may tolerate up to 5–30 mg kg^{-1} of copper (Cu), a metal that is required for plant growth. Additionally, excess Cu in plants causes oxidative stress by generating reactive oxygen species (ROS) that are detrimental to the plants. Fe shortage in crops, particularly on calcareous soils, leads to decreased vegetative growth, yield, and quality losses[37]. In plants, Mn shortage mostly affects photosystem II. Mn shortage causes destabilization of PSII super- and subcomplexes. Manganese (Mn) is an important plant micronutrient that acts as a catalyst in the Oxygen-Evolving Complex (OEC) of photosystem II. However, Mn deficiency often goes unnoticed, concealing the scope and gravity of the issue that lowers crop productivity in many regions worldwide[38].

Studies have shown that compared to monometallic nanoparticles (MNPs), bimetallic nanoparticles (BNPs) have higher antimicrobial activity against Gram-positive as well as Gram-negative microbes [39]. Ag-Pd BNPs made from *Terminalia chebula* fruit extract have been shown by Sivamaruthi et al.[40] to exhibit exceptional antibacterial activity against *Pseudomonas aeruginosa* and Methicillin-Resistant *Staphylococcus aureus* (MRSA). Nanoscale materials can be monometallic, bimetallic, trimetallic, or core-shell[43]. A combination of three different metals produces trimetallic nanoparticles, which are considered more professional than bimetallic nanoparticles [43]. In this regard, it should be noted that the effect of a nanoparticle can vary depending on the type of soil, considering variables such as the presence of organic matter in the solid or dissolved phase, as well as inorganic components, all of which can have a significant impact on the behaviour of these particles. Amongst other green synthesis methods, Microbe-mediated green nanoparticle synthesis is very common as such bacteria and fungi produce enzymes that function as capping and reducing agents. However, it takes a lot of effort and sophisticated techniques to develop these microbial species. Compared to bacteria, plants are more readily available, less expensive, and better for the environment. Moreover, inadequate nanoparticle stability may arise from biomolecule-mediated methods[48]. Extracts from plants can be employed as efficient synthetic precursors to get around these drawbacks. According to Nazar et al.[49] this technique uses phytochemicals found in tissue from plants as chelating, stabilizing, reducing, and capping agents. Northeast India is well situated where the Himalayas, the Indian subcontinent, and the Indo-Burma region converge. The region has significant levels of rainfall and humidity, especially during the monsoon season. These climatic conditions, combined with moderate temperatures throughout the year, foster lush vegetation and create suitable habitats for a variety of plant species to thrive.

Owing in part to their small size, the use of nanoparticles presents many environmental risks, such as their ease of dispersion and transport, their capacity to cause ecotoxicity, their persistence in the environment, their capacity to accumulate in higher creatures, and the potential for process reversibility. These properties have the potential to cause environmental concerns, necessitating additional research into the toxicity and ecotoxicity of various nanoparticles on aquatic and terrestrial creatures in the food chain. As a result, risk assessment studies are required to determine the potential effects on non-target organisms, as well as their importance in maintaining healthy soils and crop yields.

With the increasing strain of the population and the absence of employment opportunities in other industries, the pressure on the agricultural sector is expanding rapidly. This condition leads to increased agricultural activity and fragmentation of land holdings thus pressurizing urban populations to cultivate their foods in their small home gardens and or to adopt hydroponic farming. Hydroponic farming has various advantages over regular soil agriculture. For starters, it provides for exact fertilizer administration, which results in higher crop yields and faster growth rates. Furthermore, hydroponic systems require substantially less water than traditional growing methods, making them more environmentally friendly. Furthermore, hydroponic farming can be used in regions with low soil quality or limited arable land, creating prospects for urban agriculture and vertical farming. Finally, the absence of soil removes the possibility of soil-borne pests and diseases, therefore minimizing the need for chemical pesticides and herbicides.

Keeping all these in mind, we have adopted a sustainable agriculture method that balances environmental protection, economic viability, and social equality. Green synthesis technologies provide a more sustainable alternative to traditional chemical synthesis, reducing energy use, waste generation, and environmental contamination. We may make nanoparticles in an environmentally benign manner by using plant extracts and other natural resources, by the circular economy and resource efficiency principles. It is critical to establish the concentration at which nanoparticles may negatively affect the health of ecosystems, plant growth, and soil bacteria. By methodically assessing dose-response relationships, we can determine acceptable dosage ranges that reduce nanotoxicity while maximizing nanoparticle benefits. Nanoparticles' effects on plant physiology, growth, and yield are investigated in phytotoxicity studies. High nanoparticle concentrations can impair seed germination, root elongation, and nutrient uptake, resulting in decreased crop productivity.

1.2. Research Gaps

- ❖ The efficacy of phytochemicals in the green synthesis of nanomaterials as micronutrient substitutes in agriculture remains uncertain.
- ❖ Limited investigation exists regarding the interaction between soil physico-chemical characteristics and multi-metallic nanomaterials.
- ❖ The impacts of these nanomaterials on hydroponics and soil-borne microorganisms are subjects of debate, which compels further exploration into nanomaterial dosages and their decay effects on soil ecosystems' biological environment.

- ❖ No clear evidence was found regarding tailoring nanoparticle dosages in pulse crops, which can leverage their potential to boost plant growth, nutrient efficiency, and stress tolerance without creating phytotoxic consequences.

1.3. Key Questions

Since the identified research gaps are pointed out, the following research questions have been derived:

- ❖ To what extent do the antioxidant properties of various plant species influence the stability of nanomaterials synthesized through green methods?
- ❖ How do different types of nanomaterials impact soil-less cultivation, particularly in terms of plant growth, regulation of reactive oxygen species (ROS), maintenance of chlorophyll stability, and the absorption of nanomaterials?
- ❖ Have any metal-based nanomaterials been identified thus far that exhibit minimal to no toxicity toward soil microflora?
- ❖ Do the effects of Zinc monometallic, Zinc-Copper bimetallic, and Zinc-Copper-Iron-Manganese Quadri metallic nanomaterials vary depending on the dosage when exposed to the soil micro-environment?

1.4. Research Objectives

And, keeping all these in mind, the proposed objectives of this research were:

- ❖ Identification and efficacy assessment of indigenous herbs as reducing agents for green synthesis of Zn-based nanomaterials.
- ❖ Optimization and characterization of the synthesized Zn-based nanomaterials.
- ❖ Impacts of the synthesized nanomaterials on soil and plant health.

1.5. Hypotheses

In our study, we put forth the compelling hypothesis that the utilization of eco-friendly zinc-based nanomaterials will catalyze enhanced plant growth. Our hypothesis delves deeper into the intricate dynamics of the rhizosphere, aiming to unravel the fascinating interaction between these engineered nanoparticles and the beneficial microbes inhabiting this crucial ecosystem. By exploring this uncharted territory, we anticipate gaining valuable insights that will not only enrich our understanding of plant-microbe interactions but also pave the way for sustainable agricultural practices in the future.

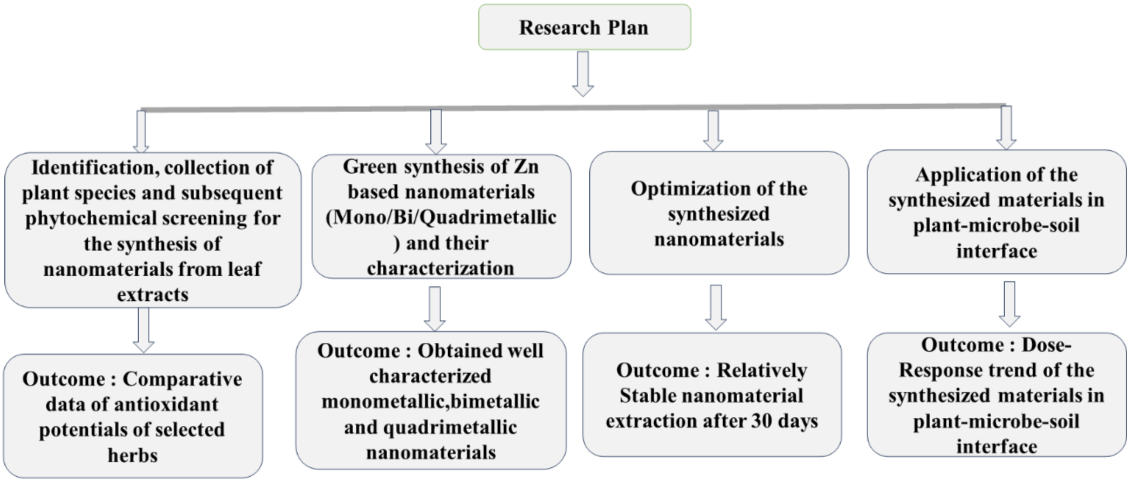

Fig.1.1. Research Plan

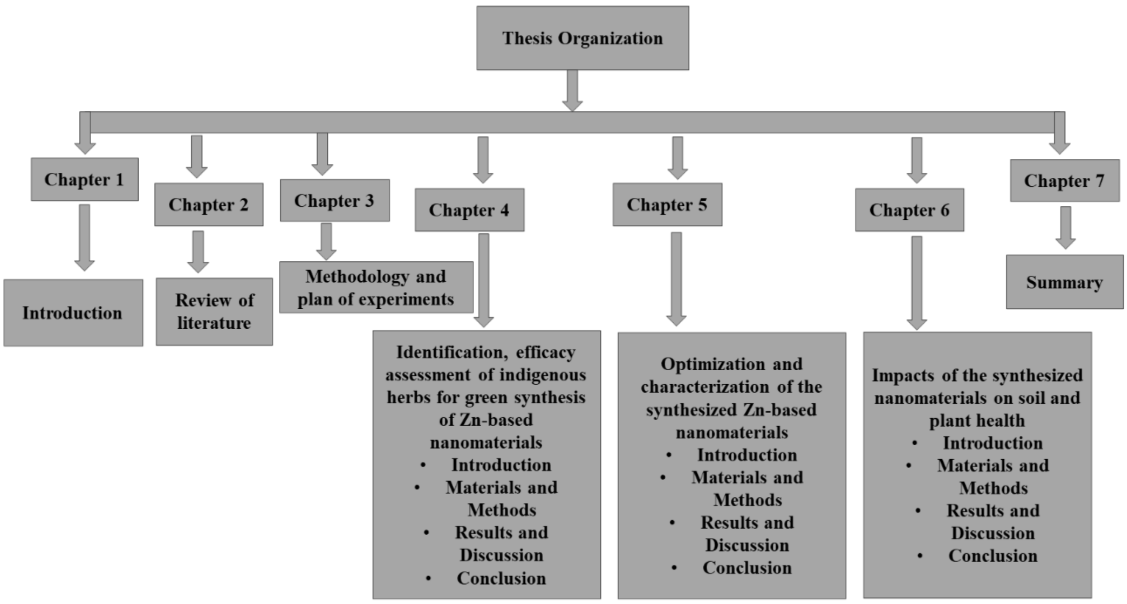

Fig. 1.2. Thesis Organization

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