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Nanofertilizers: A Novel Approach Towards a Sustainable Agriculture

Nilmini W.K.A
Faculty of Technology, University of Sri Jayewardenepura

Abstract: Application of nanotechnology and nanoscience in agriculture, improving the use efficiency of essential fertilizer nutrients to crops and enhancing crop security for agriculture's long-term sustainability. These novel fertilizers can help in obtaining higher crop yields per unit landmass. Hence, product quality can also be improved with enhanced nutrient contents and shelf life. On the other hand, the studies showing that nanoparticles can be used to enhance plant growth, many studies report on the negative impacts of nanoparticles on higher plants and the environment. Therefore, new prospects for integrating nanotechnologies into fertilizers should be explored, cognizant of any potential risk to the environment or human health. This chapter aims to highlight recent attempts taken for the intervention of nanotechnologies in the area of fertilizers and plant nutrition. We hope that nanotechnology will be transformative in the agricultural field with government and researchers' dedicated efforts to develop active nanofertilizers.

Index Terms: agriculture, nanofertilizer, nanohybrid, nanoparticles, sustainability,

1. INTRODUCTION

Fertilizers are natural or man-made products which applied to soil to fulfil the demand for plant nutrients. Although commercial fertilizers do their job in increasing crop yields, conventional fertilizer management's disqualifications can cause to happen terrible economic and environmental outcomes [1]. The partial of fertilizer nitrogen applied to farmland would be lost to water, air, and other processes. It would negatively affect marine ecosystems by leaching nitrates into that and releasing N-oxides into the atmosphere and polluting air [2]. Due to those factors, especially in developing countries, the manures' cost can be notable and is exactly the confining parameter for food supply. Therefore, it is essential to promote novel technologies that minimize fertilizers' cost through efficient and targeted delivery [3].

2. NANOTECHNOLOGY

Nanotechnology can be defined as the technology for design, fabrication and manipulation of nanometer-scale systems, in the scale of 1-100 nm. Particle size less than 100 nm on a scale belongs to a transitional zone between single atoms or molecules and correlative bulk material. It can show miraculous changes in the physical and chemical properties of the matter [4]. Nanotechnology has led to many innovations in fields as varied as medicine, material science, and electronics. Furthermore, nanotechnology is ubiquitous in our consumer products from textiles, to sports equipment, to electronics. Clear prospects exist for impacting agricultural productivity through the use of nanotechnology [2].

3. NANO-FERTILIZERS

Nanoscale fertilizers can be described as a powder or liquid formulations that contain a nutrient element(s) de-sized to nanoscale dimensions. Though the strict nanoscale dimensions pertain to 1–100 nm, several research publications have shown improvement in the fertilizer action for formulations containing sizes varying up to 500 nm. Nanoscale fertilizers are anticipated to be required in substantially small quantities, can exhibit high use efficiencies compared to conventional fertilizers [5], and may impart additional benefits other than enhanced productivity such as improved nutritional quality; other quality aspects including better shelf-life and dual or multiple roles as a pesticide or heavy metal scavenging agents [6].

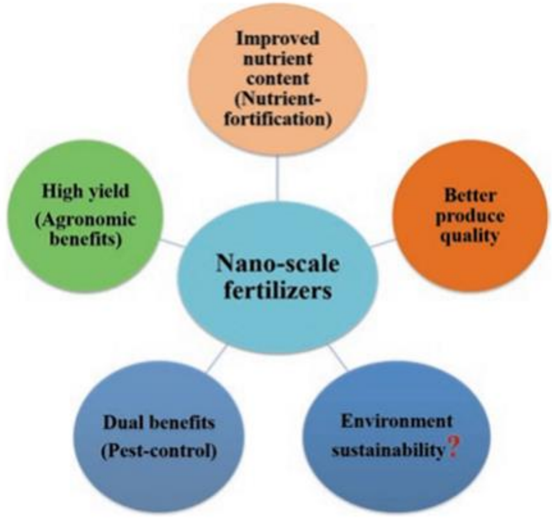

Fig. 01. Role of nanofertilizers in achieving agriculture sustainability [6]

Nanofertilizers are one potential output that could be a significant innovation for agriculture; the large surface area and small nanomaterials' small size could allow for enhanced interaction and efficient uptake of nutrients for crop fertilization. The integration of nanotechnology in fertilizer products may improve release profiles and increase uptake efficiency, leading to significant economic and environmental benefits. The increased surface area in nanomaterials can lead to increased reactivity and faster dissolution kinetics; these factors might exacerbate inefficiency problems if nanofertilizer formulations are more easily dissolved and leached into the environment [2]. However, very recently, Kottegoda et al., followed by Pabodha et al. Siriwardena et al. and Rathnaweera et al. have introduced novel technology where it reversed the releasing kinetics from fast or rapid release to slow-release. There, they used Hydroxyapatite, silica, and calcium carbonate nanoparticles incorporated with urea as a nitrogen fertilizer and come up with a slow-release fertilizer, which will be discussed in detail later [3],[7],[8],[9],[10]. Nevertheless, it is significant to realize that nanomaterials' excessive use in any field would constitute an intentional input of nanomaterials into the environment and could dramatically impact human and environmental exposure [2].

As the conventional fertilizers suffer from reduced and very low nutrient use efficiency (NUE), the nutrient elements' nanoscale will tend to alter their properties. The nanoscale fertilizers' high surface-to-volume ratio will reduce the amount of application as the nanofertilizers will be readily taken up by the plant cells on the application due to improved bioavailability resulting in improved growth and nutritional profile. Therefore, the improved uptake and availability will increase the efficiency of the nanofertilizers compared to conventional fertilizers. Concerning N and P manures notably, the nutrient losses can be substantially mitigated when used in nano form compared to conventional form. Likewise, the agronomic benefits of nanoscale micronutrient fertilizers are anticipated to be quite high [6].

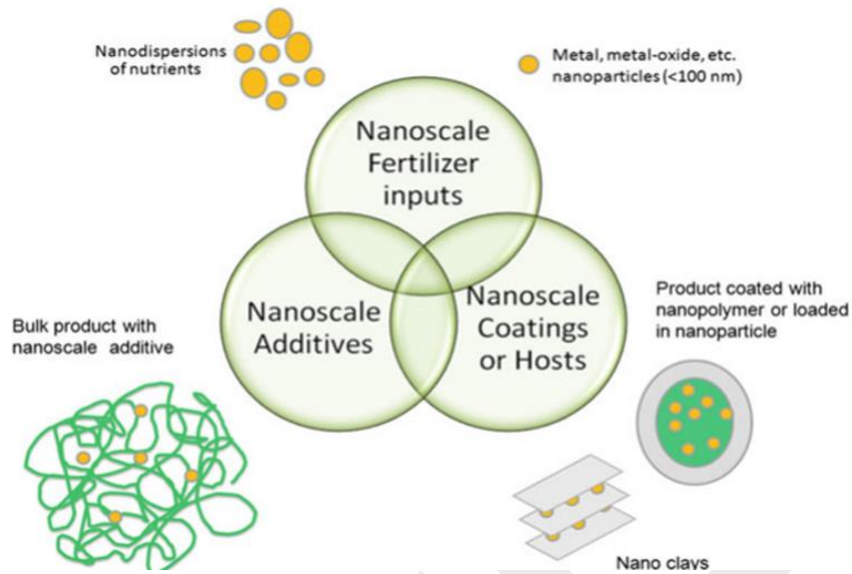

Fig. 02. Categories of fertilizer inputs: nanoscale fertilizer inputs, nanoscale additives, and nanoscale coatings or host materials[2]

There are three forms in nanotechnology implementation for fertilizers that are explored: nanoscale fertilizer inputs, nanoscale additives, and nanoscale coatings/ host materials for fertilizers (Fig. 02). These three categories do have some degree of overlap, meaning some products may fall into more than one category [2].

Nanoscale fertilizer inputs

Nanoscale fertilizer inputs have been produced in size of nanoscale as particles form or emulsions form. Fertilizer nano-inputs, containing particles made from ammonium salts, urea, peat, and other conventional fertilizers, belong to this class [2].

Nanoscale additives

In this category, a nanomaterial is included in crop rhizospheres not necessarily as the nutrient itself but perhaps as an additive to enhance plant growth, such as a binder or water retention material, or plant defense against soil pathogens [2].

Nanoscale Films and Host Materials

This category contains fertilizers and supplements that are encapsulated by nanoscale films or held in nanoscale pores or spaces within a host material. Clays finding applications fertilizer products include those such as kaolinites, smectites, halloysites, and palygorskites. These vary in terms of their chemical composition, as well as their properties, such as surface area and surface charge [2].

Nano-fertilizer synthesis approaches

Both top-down or bottom-up approaches can synthesize Nanofertilizers. The top-down approach is most commonly employed and generally involves ball milling of substrates such as zeolites for several hours to achieve nano dimension [11]. Other top-down approach techniques involve nanolithography, sputtering, thermal decomposition, and laser ablation [12]. Bottom-up approaches use constructive methods for building nanoscale particles from atoms and molecules. However, despite the improved mono dispersity features of the chemically synthesized nanofertilizers, the use of environmentally toxic compounds and expensive procedures are the prime drawbacks of the chemical synthesis techniques [6].

Application of nanotechnology in fertilizer inputs

A nanofertilizer is a product that carries nutrients to crops in one of three ways. The nutrient can be confined inside nanomaterials such as nanotubes, surface coating with a thin protective polymer film, or delivered as nanoparticles or nano-emulsions. The effectiveness of nanofertilizers may exceed the most innovative polymer-coated traditional fertilizers, which have seen little improvement in the past ten years due to a high surface area to volume ratio in nanofertilizers [13]. There are some examples in applications of nanotechnology in fertilizer inputs. Zinc–aluminium layered double-hydroxide nanocomposites have been used for the controlled release of chemical compounds that regulate plant growth. The release of nitrogen by urea hydrolysis has been controlled through the insertion of urease enzymes into nanoporous silica [13]. The development of functional nanoscale films and devices can produce significant benefits in NUE and crop production. Nanotechnology might be able to improve the performance of fertilizers in other ways rather than increase the NUE. For instance, nano size titanium dioxide has been incorporated into fertilizers as a bactericidal additive because of its photo catalytic property. Furthermore, titanium dioxide may also lead to better crop yield through nitrogen gas photo reduction [13]. For example, in a study of urea-Hydroxyapatite (urea-HA) nanohybrids for slow-release nitrogen by Kottegoda and group, they focused on synthesizing the environment-friendly nanoparticles carrying urea as the crop nutrient and discharge it in a programmed manner for use as a nanofertilizer [14].

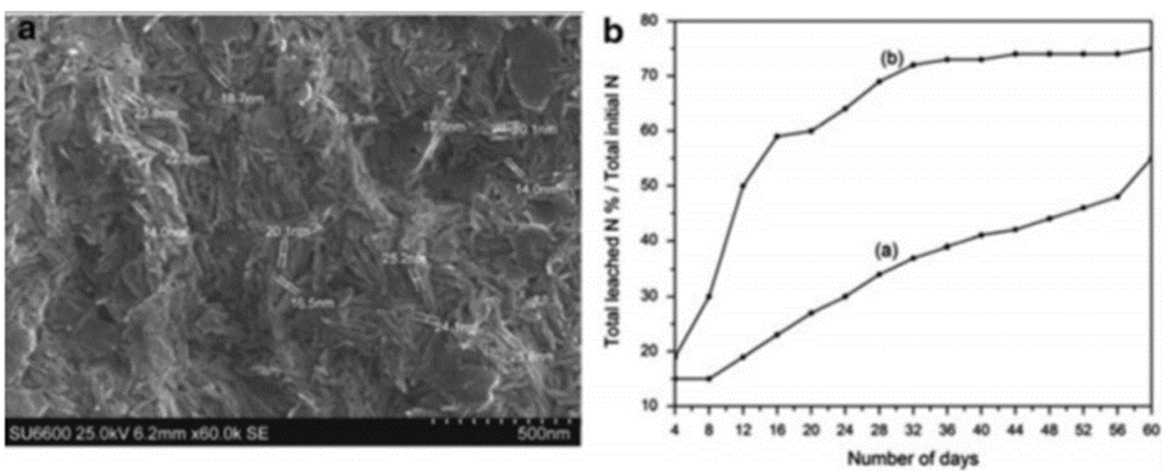

Fig.03. Hydroxyapatite nanoparticles for urea delivery. (a) SEM image of urea-modified hydroxyapatite nanoparticles. (b) Comparison of %N released over 60 days for (a) the nanofertilizer and (b) a conventional fertilizer[2]

The solubility of Urea has been reduced by incorporating it into a matrix of HA nanoparticles. This method allowed the synthesis of a urea-modified hydroxyapatite nanohybrid as fertilizer with a Urea ratio to hydroxyapatite of 6:1 by weight. Here, a nanohybrid suspension was synthesized by in situ coating of hydroxyapatite with Urea at the nanoscale. In this method, they followed the solid nanohybrid was obtained from the suspension by flash drying [15]. This group recently investigated Urea–hydroxyapatite nanohybrid as an efficient nutrient source in *Camellia sinensis (L.) Kuntze* (tea). This study chose the farmer's fields from three climatic zones (Low country, Mid country, UVA regions) in Sri Lanka. They studied Urea–HA nanohybrid fertilizer's effect on the yield quality of tea in those fields from three climatic zones for three years. Experiments were implemented using treatments with half, and full amounts of nitrogen recommendations to the tea plant supplied through both traditional Urea and nanohybrids at two and four fragments per annum. A positive effect of Urea- HA nanohybrids was more pronounced during unfavourable climatic conditions [16].

Similarly, Kottegoda and group investigated the Urea modified calcium carbonate nanohybrids as a next Generation Fertilizer. They focused on the synthesis of scalable, cost-effective, and efficient nitrogen fertilizer, which retards nitrogen solubility at a minimum of 5 times compared to pure Urea. Being a bioinspired material, calcium carbonate (CC) renders added advantages of biocompatibility and non-toxicity. Here, urea-CC nanohybrid was synthesized using an in-situ rapid carbonation method which resulted in the cubic plate-like nanoparticles that are stacked together to form pine cone-like structures. They used Fourier transform infrared spectroscopic to obtain conclusive evidence for Urea's bonding interactions with CC nanoparticles, which gave a platform for the controlled release properties of Urea. Crystallographic data of nanohybrids were obtained from powder X-ray diffraction [17].

The Kottegoda group did recent research to investigate the urea-silica nanohybrids with potential applications for slow and precise release of nitrogen. In this study, a greener, in-situ sol-gel technique was used to synthesize urea-silica nanohybrids with a high urea charge of 36% (w/w) and a filling efficiency of ~83%. The team was able to incorporate Urea into silica nanoparticles. The modification was proved to be as a result of strong interactions between urea and silica nanoparticles. However, there were no morphological changes observed during the modification. The nanocomposite exhibited slow release behaviour in water for more than ten days. The developed urea-silica nanohybrids could be utilized as a potential candidate for slow-release nitrogen fertilizers. This study focused on a novel energy-efficient synthesis of urea-silica nanohybrids with a high nitrogen loading to eliminate the drawbacks of previous works [18].

Another attempt was taken by Kottegoda and the group to investigate the effect of citric acid surface modification on hydroxyapatite nanoparticles' solubility. Here, attempts are made to synthesize citric acid surface-modified hydroxyapatite nanoparticles using the wet chemical precipitation technique. The characterization of nanohybrids was done using powder X-ray diffraction to obtain the crystallographic data, and Fourier transforms infrared spectroscopy was used to analyze functional group. Scanning electron microscopy and elemental analysis using energy dispersive X-ray diffraction spectroscopy were used to study the morphology and particle size of resulting nanohybrids. Water release studies and bioavailability studies were employed to investigate its effectiveness as a source of P by using Zea maize as the model crop. Both tests demonstrated P's increased availability from nanohybrids in the presence of an organic acid compared to pure hydroxyapatite nanoparticles and rock phosphate [19].

In recent studies on two new plant nutrient nanocomposites based on Urea coated hydroxyapatite, the efficacy and plant uptake have been demonstrated. This study reported the synthesis and plant uptake of two plant nutrient nanocomposites based on Urea coated hydroxyapatite and potassium encapsulated into nano-clay montmorillonite (MMT), and cavities present in *GliricidiaSepium* stem resulting in a wood chip containing macronutrients. According to the data they revealed, Urea fabricated into its nanoscale provides a platform for efficient fertilizer formulations [20].

4. CONCLUSION

This review aimed to develop some insight into what impact nanotechnology has made on fertilizer inputs over the short and long-term. The findings presented here indicate that nanotechnology is already beginning to impact the fertilizers in the agricultural field. Almost all of the examples within this review are still relatively early in their development (at the stage of patents and research papers). It is still unclear whether the presented and discussed nanotechnologies for fertiliser use will have any negative long-term impacts on human health or the environment. Therefore, the researchers and the regulatory bodies should focus their consideration on that matter too.

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