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PRODUCTION OF NANOFERTILIZER- A MINI REVIEW

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Abstract- Though Nanotechnology is the innovative approach to resolving multiple issues in the diverse fields in this century, lots of its applications were restricted to the engineering fields. The scope, however, now spreads its wings to the applied sciences and innovations. The present time demands more production from the agricultural sector due to which the antidotes found by the people were to use excessive amount of chemical fertilizer which culminated in the leaching and eutrophication, contamination and residual effects in the crops, long-term damage of soil and so on. This review comprehensively elaborates the functions, roles and production; biosynthesis and chemical route production of nano-fertilizers which could be applicable to many countries around the world.

Keywords— Nano-fertilizers, Encapsulation, ionic crosslinking, zeolites, smart fertilizer

I. INTRODUCTION

Nanotechnology is the noble scientific approach involving the use of materials and equipment that is capable of manipulating physical and chemical properties of substance at a molecular level [1]. On the other hand, biotechnology involves using the knowledge and techniques of biology to manipulate molecular, genetic and cellular processes to develop products and services and is used in diverse fields from medicine to agriculture [1,2]. Nanotechnology involves the manipulation of matter at the size of nanoscale ($1/10^9$ metre) by which upon the application of such prominent product in the field of agriculture not only increases the production but also provides safe food for the consumption; The ambition of nanomaterials in agriculture is to reduce the amount of spread chemicals, minimize nutrient losses in fertilization and increased yield through pest and nutrient management. Many potential benefits such as enhancement of food quality and safety, reduction of agricultural inputs, enrichment of absorbing nanoscale nutrients from the soil, etc [3]. In many countries, the ultimate aim of the agriculturist is to develop drought and pest resistant crops which also maximizes the production. In such scenario, the application of nanotechnology has gained a diverse attention. Agriculture,

food and natural resources are a part of those challenges like sustainability, susceptibility, human health, and healthy life. Nanotechnology has the prospective to improve the agriculture and food industry with novel nanotools to control rapid disease diagnostic, enhancing the capacity of plants to absorb nutrients among others. The use of nano-fertilizers gained more attention for the soil scientists and environmentalists due to capability to increase yield, reduction of pollution and improvement in the soil fertility and their prospects to making favorable environment for microorganisms [4]. Likewise synthesising nano-fertilizers via the routes this paper presents, the positive impacts were foreseen to be applicable in the agriculture and production sector in Bhutan. While Bhutan is known for the carbon negative attribute, the significant agricultural practises needs improvements from mechanization to application to production. For this purpose, this paper provides five comprehensive procedures to nano-fertilizer synthesis.

II. NANO-FERTILIZER AND THEIR ROLES

Nano-fertilizers play a vital role in the improvement of production in the wide array of crops. The nutrient use efficiency of conventional fertilizers hardly exceed 30–35 %, 18–20 %, and 35–40 % for N, P, and K respectively, which remained constant for the past several decades. Nano-fertilizers are known to release nutrients slowly and steadily for more than 30 days which may assist in improving the nutrient use efficiency without any associated ill-effects. Since the nano-fertilizers are designed to deliver slowly over a long period of time, the loss of nutrients is substantially reduced vis-a-vis environmental safety. [5]

Because of the fertilization into the soil for quite a long time, it has culminated in the depression in the crop yields due to the soil nutrient imbalance and deficiency of the organic matter. Many cases of leaching and eutrophication has been reported due to the excessive use of phosphorus and nitrogen in the form of fertilizers. According to the Royal Society, “Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale” [6]. Nowadays,



nanotechnology is progressively moved away from the experimental into the practical areas [7]. For example, the development of slow/controlled release fertilizers, conditional release of pesticides and herbicides, on the basis of nanotechnology has become critically important for promoting the development of environment friendly and sustainable agriculture. Indeed, nanotechnology has provided the feasibility of exploiting nanoscale or nanostructured materials as fertilizer carriers or controlled-release vectors for building of so-called “smart fertilizer” as new facilities to enhance nutrient use efficiency and reduce costs of environmental protection [7,8].

III. PRODUCTION OF NANO-FERTILIZER

Nano-fertilizers intended to improve the nutrient use efficiencies by exploiting the unique properties of nanoparticles. The nano-fertilizers are synthesized by fortifying nutrients singly or in combinations onto the adsorbents with nano-dimension. Both physical (top-down) and chemical (bottom-up) approaches are used to produce nanomaterials, and the targeted nutrients are loaded as it is for cationic nutrients (NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) and after surface modification for anionic nutrients (NO_3^- , PO_4^{2-} , SO_4^{2-}). [6].

Encapsulation of fertilizers within a nanoparticle is one of these new facilities which are done in three ways a) the nutrient can be encapsulated inside nano-porous materials, b) coated with a thin polymer film, or c) delivered as particles or emulsions of nano-scales dimensions [9].

A. NANO-FERTILIZER FROM BANANA PEELS

Banana peels are the organic waste rich in natural phenolic compounds antioxidants such as flavonoids, vitamins, essential amino acids, growth promoters and potassium elements which are essential for plant growth [10]. Egyptian Banana peels (William Ripe peel) were shredded and blended with tap water into which a determined quantity of potassium hydroxide were poured in and stirred for a minute to result a slurry. The alkaline blended slurry was boiled for 30 minutes and then cooled to room temperature. The cold slurry was subjected to vacuum filtration to get a clear brown filtrate and thick dark brown sludge. Hence, the clear filtrate was heated to about 70 °C, with continuous stirring at 300 rpm. After that, urea and citric acid (5% solution) were added dropwise till pH 5. Then, the obtained sludge was dried at 105 °C, then ground to fine powder (Nanofertilizer). The fertilizer constituent size ranged from 19 to 55 nm, and the histogram illustrated that the major nanoparticles were 40 nm with an average percentage of 36% while 55-nm particles were the minor size with an average percentage of 6%. The synthesized nanofertilizers contained chelated potassium, chelated iron, tryptophan, urea, amino acids, protein, and citric acid. Upon studying the germination rate in the tomato and fenugreek after application

of nano-fertilizer, their germination rate increased from 17% to 97% and 25% to 93.17% respectively in a duration of a week [11].

B. NANO-FERTILIZER VIA INCORPORATION OF ALGINATE-CHITOSAN

Potassium nano-fertilizer was synthesised by incorporating potassium in alginate-chitosan carrier via ionotropic pre-gelation was optimized to maximize potassium content and develop controlled release fertilizer. Utilizing two-level factorial design, potassium to alginate ratio, calcium chloride to alginate ratio, and pre-gelation time were determined significant [12]. Potassium nano-fertilizer was prepared on a four-step process that included the preparation of potassium-alginate solution (K-ALG), pre-gelation, stabilization, and equilibration. For the preparation of K-ALG, 117.5mL of ALG was mixed with MOP and sonicated in Elma Model S 60 H Elmasonic sonicator for 20 minutes at room temperature. On pre-gelation step, CaCl_2 was added dropwise to K-ALG to form pre-gel while sonicating at 37 kHz at RT. On stabilization step, 25 mL of Chitosan Stock Solution (CHI) was added dropwise to stabilize K-ALG while stirring at 600 rpm for 90 minutes at RT. The K-ALG- CHI mixture was stirred for another 30 minutes for better homogenization. Then, the K-ALG-CHI was allowed to stand for 24 hours at room temperature to complete the chemical reaction. After that, the pinkish viscous solution was oven-dried at 70°C for 1 hour to obtain solid formulated fertilizer. Characterization showed that potassium was successfully incorporated. Moreover, controlled release fertilizer can be attributed as only 14.6 % K was released in Britton-Robinson buffer solution after 7 days.

C. NANO-FERTILIZER USING FOOD GRADE KAPPA-CARRAGEENAN CARRIER

Potassium nano-fertilizer was synthesised using food grade kappa-carrageenan as carrier and fertilizer grade muriate of potash (MOP) through ionic crosslinking which involves linking of the K^+ ion with carrageenan's SO_3^- group to form gel. The increased Total Potassium content was observed at increased potassium-to-carrageenan ratio which was analyzed using flame photometry. After 48 hours, muriate of potash almost reached the maximum Total Potassium it is available to be released from the fertilizer. Meanwhile, the potassium-carrageenan fertilizer would still be capable to release more potassium. Relative to the conventional MOP, a slower accumulated release of potassium was observed for the synthesized potassium-carrageenan fertilizer. Because of the wide availability of carrageenan and its properties, it is considered a good carrier for delivery systems especially with potassium because of its effective cross-linking compatibility [13].



D. BIOSYNTHESIS OF ZINC NANO-FERTILIZERS

Zinc is one of the essential nutrients required for the plant growth. Its important role can be adjudged as it controls the synthesis of indole acetic acid, a phytohormone which intensely regulates the plant growth. Besides, it is also necessary for chlorophyll synthesis and carbohydrate formation [14]. Zinc is not only a structural component in the phosphatase enzyme but also plays a crucial role in the native phosphorus nutrient mobilization in the rhizosphere [15, 16]. Zinc nano-particles which was then used as a nano-fertilizer was developed via a biosynthesis route [17]; The fungi, *R. bataticola* TFR-6 was grown-up in 250 mL Erlenmeyer flask containing 100 mL Potato Dextrose (PD) broth medium. Medium pH was adjusted to 5.8 and culture was subjected to agitation at 150 rpm at 28°C for 72 h. After incubation, fungal balls of mycelia were filtered and washed in distilled water. Harvested mycelia (20g wet weight) was resuspended in 100mL sterile water and rotated at 150rpm at 28°C for 12 h. The product was then filtered through a 0.45 micron membrane to obtain a cell free filtrate. Cell free filtrate was used to prepare salt solution of zinc oxide of 0.1 mM in erlenmeyer flask. Then the entire mixture was kept on a rotary shaker for 150rpm at 28°C for 4 hours. The bio-transformed product was collected periodically (1h time interval). The growth rate of pearl millet (*Pennisetum americanum*) was studied for which significant improvement in growth was noticed: shoot length 15.1%, root length 4.2%, root area 24.2% in six weeks old plant. The grain yield of crop maturity was found to 37.7% due to application of nano-fertilizer.

E. NANO-FERTILIZER VIA SURFACE MODIFICATION OF ZEOLITES

Source of nitrogen include ammonia, diammonium phosphate, ammonium nitrate, ammonium sulphate, calcium cyanamide, calcium nitrate, sodium nitrate and urea [18]. In most of the cases N is lost in the atmosphere by volatilization, denitrification, leaching and run off. Hexadecyltrimethylammonium bromide (HDTMABr) was used for the surfactant modification of zeolite. A pre-weighed quantity of zeolite was mixed with (HDTMABr) in 1:100 ratio (solid to liquid). The mixture was agitated for 7-8 h at 150 rpm on an orbital shaker and then filtered. The solid residue was washed with double-distilled deionized water and oven dried for 4-6h. The synthesized Surfactant Modified Zeolite (SMZ) was then mechanically ground with a mortar and pestle into fine particles. To prepare nano fertilizer, required quantities (~170 g) of SMZ were stirred with a 1.0 M solution of $(\text{NH}_4)_2\text{SO}_4$ for 8 h and filtered, washed three times with deionized water, and oven dried. The solid: liquid ratio was 1:10 for the synthesis of nitrogen loaded zeolites.

IV. FUNCTIONING OF NANO-FERTILIZERS.

Nano-fertilizers combines with the nano-devices in order to synchronize the release of fertilizer-N and -P with their uptake by crops, preventing undesirable nutrient losses to the soil, water and air via direct internalization by crop and avoiding the interaction of nutrients with soil, microorganisms, water and air [19].

Nanostructured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production, and save fertilizer resource. Controlled release modes have properties of both release rate and release pattern of nutrients for water-soluble fertilizers might be precisely controlled through encapsulation in envelope forms of semi-permeable membranes coated by resin-polymer, waxes and sulphur. Effective duration of nutrient release has desirable property of Nanostructured formulation, it can extend effective duration of nutrient supply of fertilizers into soil. Nanostructured formulation can reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking.

V. NANOPOROUS ZEOLITES

Nano-clays and zeolites that are a group of naturally occurring minerals with a honeycomb-like layered crystal structure are other strategies for increasing fertilizer use efficiency [20]. Its network can be filled with nitrogen, potassium, phosphorous, calcium and a complete set of minor and trace nutrients. So acts as a nutrients supply that are slowly released "on demand". However, it is stated that the main application of zeolites in agriculture is in nitrogen capture, storage and slow release [21]. Application of soluble Nitrogen fertilizers is one of the major reasons for groundwater contamination. Nitrogen releasing dynamics in the absorbed form (in zeolites) is much slower than for the ionic form. Urea- fertilized zeolite chips, can be used as slow release nitrogen fertilizers [22]. Ammonium-charged zeolites have shown their capacity to raise the solubility of phosphate minerals and thus goes to improved phosphorus uptake and yield of crop plants. Studies conducted to check solubility and cation-exchange in mixtures of rock phosphate and NH_4^+ and K-saturated clinoptilolite showed that mixtures of zeolite and phosphate rock have the potential to provide slow-release fertilization of plants in synthetic soils by dissolution and ion-exchange reactions. The possibility of using surfactant-modified zeolite using hexadecyltrimethylammonium as fertilizer carrier to control nitrate release was demonstrated and deduced that surfactant-modified zeolite is a suitable sorbent for nitrate, since slow release of nitrate is achievable. These dual properties propose that surfactant-modified zeolite has the potential to be used as fertilizer carrier to control the release of nitrate and other anions [23].



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