International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

A review on immobilization techniques for fertilizer

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Abstract

Fertilizers (also called plant food elements) are materials produced to supply macro and micro-nutrients to the plant in a readily available form. Here we provide brief information on recent developments in fertilizer (mainly N, and P) production and their use, improvement in nutrient efficiency, and the immobilization of fertilizers to minimize environmental impact. There are diverse physical, industrial, and natural strategies existing for the fertilizer immobilization, for example, adsorption strategy, exemplification technique, bio-based epoxy covered urea technique, starch-based superabsorbent polymer, graphene oxide technique, enzymatic technique, and microbial strategy. All strategies have distinctive applications since all these strategies can't relevant for all smaller scale and macronutrient, so a unique strategy is used to immobilize the constituent, for instance, graphene technique is used for phosphorus and give considerably more efficient results when compared to the rest of other strategies. Organic strategy is likewise used, yet condition for response is kept up so troublesome like pH and temperature, so natural techniques are used in this case. Natural burdens become a noteworthy issue and profitability diminishes at an amazing rate. Our trust in synthetic fertilizers and pesticides fortifies but synthetic compounds are hazardous for human utilization as well as for environment. However, fertilizer immobilization can help take care of the issue of sustaining an expansion of the worldwide population when horticulture is confronting different natural anxieties. It is imperative to comprehend the useful parts of immobilization and execute their applications in present day horticultural practices. The new innovation worked with the incredible assets of atomic biotechnology can upgrade the natural pathways of phytohormone creation. When distinguished and exchanged to valuable fertilizer, immobilization of fertilizer, these advancements can help give alleviation from natural burden.

Key words: Fertilizers, Immobilization, Nutrient, Soil, Physical Methods

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1. Introduction

The interest in the land and the knowledge of its fertility level is increasing day by day, since the land is the first natural wealth that provides food for all living things. Research has been conducted all over the world to preserve and raise the soil fertility in order to increase production per unit area to enhance the general national income. The soil is a characteristic assortment of fine stones, minerals and natural components. Sand, mud and natural material help with giving tilting, air circulation and good drinking water rates, however, the soil should be supplied with sufficient plant sustenance to keep up the solid development rate. Manures (additionally called plant nourishment components) are materials made to provide the plants with the vital components in an effectively open structure for their use. Seventeen components are known for their importance in the development and improvement of plant growth. Three of the seventeen vital components are carbon, hydrogen and oxygen are obtained from the air and water. The rest of the components are utilized by the plant ought to be starting from the earliest stage from additional fertilizer materials. In order to fulfill the plants nutrients demand, natural or synthetic fertilizers are used. The fertilizers are classified into a number of classes; "Multi-supplement fertilizers" (or "complex manures") which provides the plants with at least two components, for instance, nitrogen and phosphorus (NP). However, twofold fertilizers include NP, nitrogen and potassium (NK), and phosphorus and potassium (PK). Now a days most of the applied fertilizers are NPK tradition, although Australia's tradition, following a NPKS framework which adds sulfur to NPK tradition, some uses natural material with the addition of elements such as P and K [1]. The rapid release of fertilizers uses ammonium compounds, usually ammonium sulfate or ammonium phosphate and pure urea. While nitrogen is quickly dissolved in water and is almost immediately available to the roots, therefor they make a quick, but relatively short life and green-up response. The measure of a fertilizer required for grass, trees, bushes and palms depends on the measure of nitrogen which is expected to look after ordinary, sound development without consumption by the plants. The measure of fertilizer, given in pounds of nitrogen per 1000 sq. Ft., as indicated in the following equation, is known as the prescribed rate that is subjected to the level of absolute nitrogen and furthermore the nitrogen framing type [2].

$$\textbf{Pounds of fertilizers required} = \frac{\textbf{Recommended amount of N}}{\textbf{\%N in fertilizer}} \times \frac{\textbf{Total area to be treated}}{\textbf{1000 sq. ft.}}$$

At the present time, the main obstacles facing the farmer regarding to fertilizers are that chemicals get leached into the soil and not available to the plant for longer time, as well as it causes contamination to the soil [3]. Fertilizer Immobilization represents one of the promising methods to overcome these problems. In the following, different immobilization techniques are discussed in details.

2. Immobilization of fertilizers

Immobilization in soil science is defined as the conversion of inorganic mixes into organic mixes by microorganisms or plants to avoid their over access to plants. Immobilization is the inverse of mineralization. There are various methods to immobilize fertilizers so that to do their proper nutritional role in plants (Table 1).

3. Techniques for immobilization of fertilizer

Ex-situ immobilization of fertilizers is the best way to avoid the soils being contaminated by the leaching of chemicals from the fertilizers to the plants. Various immobilization techniques are illustrated in Figure 1. These methods are applied to areas where high contamination in soil should be removed from its source location, but its storage is linked with a high ecological risk (e.g., in the case of radio nuclide). The advantages of the Ex-situ methods are (i) quick and easy use and (ii) relatively low cost of investment and operations. Disadvantages include (i) highly corrosive to environment [4-5], (ii) building a large amount of solid wastes (twice as large as volume after processing), (iii) the byproduct should be stored on a special landfill site, (iv) in case of changing physical condition to the physical product or around it, there is serious danger of releasing additional environmental contamination, and (v) the permanent control of the remaining waste is required. In the In-situ immobilization methods, adjusting fixing agents are applied to unchanged soil. The advantages of the In-situ methods are (i) very low invasively, (ii) simplicity and speed, (iii) relatively inexpensive, (iv) small amounts of waste products, (v) high public acceptance, and (vi) inorganic pollutants. Disadvantages of in-situ immobilization methods are (i) it is considered as a temporary solution (the contaminants are still in the atmosphere), (ii) activating pollutants may occur when the chemical properties are able to change to other forms, (iii) the reclamation process is applied only to the surface layer of the soil (30-50 cm), and permanent monitoring is required [6]. The organic and inorganic alterations are regularly used for immobilization innovation to quicken the metallurgical penetrability and danger of the dirt. Basically, the major role of immobilizing alterations is to convert the primary ground metals to the more geochemically stable state through sorption, precipitation, and intricacy forms.

3.1. Physical technique

3.1.1. Adsorption method

When large amounts of phosphate are released, this can be turned into a genuine wellspring of contamination in beach front or lake waters, bringing about unreasonable arise of photosynthetic sea-going green growth and eventually turned into the primary driver of eutrophication. Adsorption is to some degree progressively successful and affordable for the expulsion of phosphate in these techniques. Considering their eco-companion and minimal effort, the utilization of these bio-sorbents spent as moderate discharge of phosphate fertilizer that will be increasingly dependable for some time later. In a research, virgin sugarcane bagasse was made of very powerful bio-gum for the extraction of phosphate, then the soaked bio-sorbent was utilized as a moderate discharge phosphate manure in water or soil. Lung rounded forces are changed by four ammonium bunches by uniting epiclorohydrin, ethanediamine, and trim ethylamine, shaping quaternary ammonium-based sugarcane bagasse (QA-SB) [7].

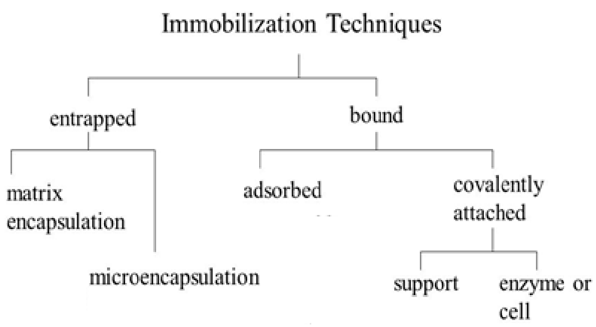

Figure 1: Immobilization techniques

3.1.1.1. Advantages and disadvantages of QA-SB adsorption method

The phosphate adsorption in the QA-SB increases with the elevation in temperature, the adsorption is ideal at a pH of 4.33-5.88. Phosphate is caught by the QA-SB in a fixed-bed segment determined at 18.9-21.4 mg/g at the base of Cl^- or NO_3^- (100 mg/L). This outcome showed the exothermic idea of the phosphate take-up by QA-SB. The outcome demonstrated that the phosphate stacked in the soaked QA-SB could be proficiently desorbed. To attain a moderate phosphate stacked in watery arrangement, soaking should be done persistently for 12 days with 43.6% of charged phosphate (11.6 mg/g) to be discharged. In contrast, phosphate (7.4 mg/g) released in soil almost reached equilibrium within 4 d, accounting for releasing only 27.8%

of laden phosphate.

3.1.2. Encapsulation method

Nano scale-level procedures showed that, because of the high surface area ratio, nano-manures are more compelling than considerably polymer-covered customary moderate discharge fertilizer. In this regard, a research has been conducted in order to find out moderate discharge fertilizer piece depending on urea-adjusted hydroxyapatite (HA) (Ca_{10} $(PO_4)_6$ nanoparticles embodied in pits present in delicate wood. Nanoparticles are appraised as one of the noticeable applicants in rural applications, which can give supplement phosphorus.

HA nanoparticles are joined with wet synthetic techniques and surfaces are adjusted by urea, the most broadly utilized water-dissolvable nitrogen supplement plant, and a synthesis of the manure is created by embodiment of urea-altered HA nanoparticles in the smaller scale/nano permeable pits of the small stem of Glyricidiasepium. The response occurs as indicated by the accompanying condition.

$$\mathbf{6H_3PO_4 + 10Ca(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O}$$

The best weight required to accomplish the most astounding heap of N. When the HA-adjusted core urea is put away inside the pits present on the wood, these cavities become repositories for in the capacity of urea altered HA nanoparticles. At the point when the bits of embodied G-sepium are joined to groundwater, urea that is restricted to expansive vascular channels were discharged at around four days pursued by the arrival of low and non-uniform amounts up to around the day thirty.

3.2. Chemical technique

3.2.1. Starch-based superabsorbent polymer

Farming promotes the quickly developing overall populace with sustenance, dress, and different necessities of day by day life, as well as fundamental for the ascent of human progress. In order to achieve the desired development for nourishment and other agro-items, in the course of recent decades, a lot of various manure (nitrogen, phosphorus, and potassium) have been connected to improve crop yields. In any case, while connected straightforwardly, the productivity of most manures, particularly nitrogen shapes, are enormously diminished because of volatilization and filtering of supplements. Additionally, it causes natural contamination and medical problems because of water eutrophication and unsafe outflows of (NH_3, N_2O and so forth.) that are coming about because of the hydrolysis of supplements and the impact of microorganisms.

By utilizing acrylamide (AM) and starch from three natural sources (corn, potato and cassava), starch-superabsorbent polymers (SAPs) such as starch-g-polyacrylamides are joined with a twin-move blender with ceric ammonium nitrate (CAN) as the activity and N, N'-methylene bisacrylamide (N-MBA) as cross-linker. The impacts of Natural SAP-based structures and structures are examined. At that point, a moderate discharge of fertilizer like urea particles within the sight of an EC covered first and the starch-SAP second, were readied, and its dirt holes conduct was assessed.

3.2.1.1. Preparation of starch-SAPs

The progression of starch-SAP tests that utilize starch from three herbal sources (eg Labyrinth, potato and cassava) are readied utilizing an adjusted twin-move Hake blender that gives high shear worry to make of high consistency materials.

3.2.1.2. Behavior of slow-release fertilizer in soil

Lead discharge of pure urea particles and their covered generation ground occurs at encompassing temperatures. When used in a wet soil for 24 h, 95% supplement, nitrogen was discharged from uncoated urea granules, though particles with EC covered demonstrated a known decrease in the measure of supplement discharge (around 60%), while the hydrophobic EC confines the infiltration of water atoms into the urea center. The SAP ceramics layer demonstrated a decent moderate dislodging of the property with a discharge estimation of 40% at 24 h and may keep on discharging supplement for quite a while (ca 70 % to 96 h in current work) showing a moderate discharge conduct for soil manure grains. In view of these effects, we recommend making changes in the SAP structure and assimilation of the property which are essential to change the conduct of supplement rich nourishments.

3.2.1.3. Advantages and disadvantages Starch-SAP

The fast arrival of excrement to the water maintenance limit is effectively created by utilizing ethyl cellulose as inner layer and starch-SAP as external layer. The varieties in nitrogen discharge conduct from manure can be credited to organic starch sources, which provides starch-SAP with various water permeable properties by size of fractals, for example, gels on the nano scale and the breadth of frameworks on the micron scale in the 3D system of starch-SAPs. The progression in the measurement of the fractal gel and the decrease in the span of the lattice is particularly alluring for increasing the ingestion rate of retaining water and improving the creation of moderate outflow of manure.

3.2.2. Graphene oxide method

Utilizations of manures, as a basic piece of horticulture, are in charge of roughly 50% of the world's harvest generation development every year, this ratio does not meet our demand; the powerlessness to utilize fertilizer in horticulture demonstrates the presence of ammonium and nitrogen in soil, water, and alkali noticeable all around. Furthermore, P is in charge of the eutrophication of groundwater, waterways, lakes and marine frameworks that are perceived as a genuine danger to biodiversity and different capacities in the sea-going biological system. When softening manures added to soils, a progression of responses may happen, for example, trade/adsorption, billows of mists and rot, with soil limits Fe-oxides, mud and real particles like calcium by changing its destiny and bioavailability (eupkeep, obligation and fix). Coal materials are a standout amongst the most utilized materials for agrarian and natural applications. The way that they are practical, ecologically well-disposed and has the attractive physical compound attributes makes them perfect material for modern scale applications. Bio-burn is a kind of carbonaceous material, generally made of biomass pyrolysis, and its composites are as of now being explored for P recuperation and recuperation from waste water. Today, GN and its oxidized structure, graphene oxide (GO), with a scope of responsive oxygen utilitarian gatherings and a high explicit surface, has been affirmed in numerous investigations as non-poisonous and biocompatible materials. The principal phosphate (PO_4^{-3}) was utilized as an anion show and the GO's capacity to give a moderate discharge plate structure for P was surveyed.

3.2.2.1. GO-Fe (III) complex preparation

Around 500 mg of GO were ultra-sonicated in 500 mL of deionized water to acquire homogeneous scattering. At that point, a suitable mass of $FeCl_3$ was broken down in a base measure of deionized water, then gradually added to GO under an enthusiastic blend to give 1: 1 (m/m) GO: Fe proportion. The blend was mixed for 1 h and centrifuged at 2950g for 30 minutes. After centrifugation the supernatant was evacuated, and the GO-Fe composite buildup was dried in a stove at 50 ° C medium-term.

3.2.2.2. P onto the GO-Fe (III) complex

For the stacking of P to the GO-Fe composite, potassium dihydrogen phosphate (KH_2PO_4) is utilized as a wellspring of solvent P. The GO-Fe composite suspended in deionized water at a centralization of 1 mg/mL was ultra-sonicated for 1 h and afterward included KH_2PO_4 salt, under sound blending to accomplish 150 mg P/L.

3.2.2.3. Advantage and Disadvantage Graphene oxide method

Begin from the minimal effort and common regular material, graphite; a straightforward course of framing the novel carbonaceous material, GO-Fe was acquired. The GO-Fe composite was observed to be viable in keeping up to 5% P over it, P discharged gradually in arrangement contrasted with business Guide manure. The perception and substance investigation of P dispersion in three soils indicated that over 99% of P was discharged from GO-Fe-P that kept up in the composite or was close to the region of the work site, which demonstrates the moderate properties of discharge. It suggests that GO-Fe-P composites are promising transporters for P that can empower better utilization of the additional supplement of plants without bad ecological effects.

3.2.3. Bio-based epoxy coated urea method

Epoxy gums with flexible thermosetting polymers with superb properties of high bond quality and great water opposition, have broad applications, for example, glues and coatings. The bio-based epoxy saps with various structures and properties have as of late been orchestrated by sustainable materials, for example, cardanol lignin. Bagasse buildups of sugar stick is a characteristic inexhaustible material comprising of three principle segments, for example, cellulose, lignin, and hemi-cellulose.

3.2.3.1. Production of liquefied bagasse (LB)

A specific measure of dissolvable and sulfuric corrosive (3% dissolvable) was added to the carafe. At the point when liquefaction solvents achieve 150 ° C, the bagasse powder is bit by bit added to the cup in the mass proportion of fluid to strong. The blend was mixed at 150 ° C for 120 min to accomplish the fluid. At that point, the carafe is promptly evacuated and cooled to room temperature. The hydroxyl number of LB is likewise decided (305.5 mg KOH/g).

3.2.3.2. Production of bio-based epoxy coated urea (EPCU)

liquefied bagasse and BDE together with NNDB at 80°C for 15 min in various Mo/CH (O) CH mole proportions (1: 2, 1: 3, 1: 4) to get the covering fluid and the relating epoxy covered urea is marked EPCU1, EPCU2, EPCU3, individually. Urea particles are warmed at 50-70 ° C in a turning drum. The fluid covering drops over the urea particles on the rotating drum and is recuperated around 5 min. in triethylene tetraamine (TETA) In the wake of splashing the deliberate amount of fluid covering, the last bio-based epoxy covered urea (EPCU) item was gotten, then cooled at room temperature, and put away in sacks.

3.2.3.3. Nutritive release behavior of EPCU

Nitrogen (N) emanates the conduct of EPCUs. Different discharge bends of EPCUs demonstrate distinctive supplement discharge rates of EPCUs. The N introductory discharge rates (on the main day) are 67.21%, 60.89%, and 45.22% for EPCU1-1, EPCU1-2 and EPCU1-3 respectively. The N discharge length of the EPCUs has increased from 3 to 5 and 10 days when the covering material has extended to 3.5, 5.5, and 7.5% respectively. Unmistakably, these coatings show ineffectively controlled discharge properties. With expanding BDE content in EPCU covering materials, the N beginning discharge rates at 24h were 67.21%, 78.22%, and 42.55% for EPCU1 - 1, EPCU2-1 and EPCU3-1, separately.

3.2.3.4. Advantage and disadvantage of bio-based epoxy coated urea method

Bio-based epoxy was effectively made for utilizing melted bagasse as a green covering material for CRF. Our outcomes have demonstrated plainly that the EPCU properties and structures of covering material are influenced by various LB proportion mating in BDE. The trial information showed that EPCU3 has exhibited a higher thickness structure, better warm security, and higher water contact point contrasted with EPCU1 and EPCU2. Furthermore, 7.5% EPCU3 contains longer nitrogen discharge life time (60d) contrasted with different EPCUs, which demonstrates prevalent controlled discharge attributes. This work gives new methodologies for planning a superior CRF cost proportion on bio-based covering materials from inexhaustible sources later on.

3.3. Biological Methods

3.3.1. Enzymatic Method

The natural compound formation by Wohler from inorganic materials has a principle importance in production of urea ever [8]. Urea is additionally utilized in vast amounts as fertilizer. In nature it is hydrolyzed by a chemical urease (urea amidohydrolase EC3.5.1.5), a multi-subunit nickel subordinate metalloenzyme that catalyzes the hydrolysis of urea at a rate of roughly un-catalyzed response rate. It is qualified to express that the last procedure continues through unexpected instruments in comparison to this catalyzed urease. These record types are vast in absolute utilization of nitrogen manures around the world. Its application is joined by substantial smelling salts misfortunes, discharged from the activity of bacterial ureases by its volatilization [9]. Urea is a compound that is difficult to dissolve in water, including soil water. In this way, it tends to be "joined" into the dirt by enough downpour or water system (1/2 inches are normally proposed). Else, it ought to be incorporated by cultivating to lessen misfortunes. Land responses to urea when attached to the ground and rejected by water or dispersion, it is liable to the loss of volatilization of N. It happens as urea experiences hydrolysis in carbon dioxide and alkali

$$(NH_2)\,2CO + H_2O \rightarrow CO_2 + 2\,(NH_3)$$

Urea hydrolysis is catalyzed by urease, an enzymatic protein made by numerous microscopic organisms and a few plants, and in this manner in every aspect of soils. The organic corruption of urea by urease discharging N for the utilization of the plant additionally changes volatilization (as NH_3, a gas) contingent upon whether the response happens on the ground or on the ground. when this occurs inside the ground, smelling salts rapidly reacts to groundwater in the form of NH_4^+, which is bound to the ground. If this happens on the ground, vaporous smelling salts are effectively lost noticeable all around. In case that the fluid plant is bottomless over the dirt, it builds the bacterial populace, urease fixation and loss of urea increment.

3.3.2. Slow release fertilizers (SRF) in soils with various microbial activity

Moderate fertilizer discharge can be created by the response of urea to different aldehydes. Their efficacy is in discharging nitrogen gradually faster than those were utilized before. Accordingly, plants are expected to uptake nitrogen viably and effectively. Besides, nitrate draining, lesser application costs and appropriate accessibility of Nitrogen in the developing time of plants is additionally seen as its valuable outcomes[10]. Among SRFs, Urea-formaldehyde (UF), Isobutylidenediurea (IBDU) and Crotonylidenediurea (CDU) have observed. Urea in UF is acquired by responding urea to formaldehyde and comprises in a blend of polymer chains of fluctuating lengths. The corruption and consequent N discharge from UF are driven by the size and action of soil microflora and by those elements that have an impact on the microbial movement similar to soil dampness and temperature. CDU which is a ring-organized compound, is created by the buildup of urea with acidic aldehyde[11]. Both the microbial movement and the hydrolysis lead to the corruption of manure. Moderate discharge manures have been generally considered under various temperature and soil dampness routines. For instance, on account of UF, an unmistakable relation between microbial movement and nitrogen discharge, higher nitrogen discharge in soil with higher microbial action, was seen under ideal research conditions. Be that as it may, the outcomes are not quite the same as those detailed in different examinations where both the size and action of the dirt microflora have no noteworthy impact on the arrival of nitrogen. Furthermore, because of the role of pH in the modification of hydrolysis responses, the arrival of N discharge from SRF under various pH soil has suggestions for their execution on various kinds of soil. The point of this investigation was along these lines to all the more likely see such connections by deciding the nitrogen discharge from UF, IBDU and CDU fertilizers in soils with various microbial action. All the more explicitly, being nitrogen discharge from UF mostly determined by microbial movement, we theorized a quicker nitrogen discharge from this fertilizer in soils with higher microbial action. As the relation between microbial soil movement and nitrogen discharge from Urea formaldehyde, it is conceivable that the arrival of nitrogen from the fertilizer happens fundamentally because of the action of microorganisms that produce UF weak chemicals. In this way, soil microbial action is by all accounts as a poor marker of UF conduct in soils. The pH impact on IBDU debasement is of optional significance in light of the fact that higher N arrivals of acidic conditions are not watched. Be that as it may, the nitrogen discharge from CDU isn't legitimately influenced by the microbial action or the pH of the dirt. Along these lines, in spite of the fact that we perceive the significance of germ movement in nitrogen discharge from moderate outflow of manures, the consequences of the present investigation show that the size and large action of the dirt microflora have peripheral effect on fertilizer harm.

Table:1 Various methods of Immobilization fertilizers

Classification	Methods	Advantages	Disadvantages

Physical	Adsorption Method	In adsorption method phosphorus is available for long time as nutrient for plant as compare to other.	The release of phosphorous from QA-SB as exothermic processes.
	Encapsulation method	Bentonite is potentially potential applied as a filler to enhance compatibility, flexibility, and structural. The properties of polymer beads and bentonite are used to release the sloe of bacterial fertilizers.	This method is less applicable as compare to adsorption method.
Chemical	Starch-based superabsorbent polymer	This method is easier, more applicable as low cost method.	This method not gives more good result as compare other chemical method.
	Graphene oxide method	Synthetic route is simple and more useful. It show 99% slow release fertilizer	Complex consumption is more and PH And Temperature is more effect
	Bio-based epoxy coated urea method	Preparation of proxy method is difficult but more useful and show favorable result.	Substrate consumption more and expensive method
Biological	Enzymetic method	Commonly useful and easily approachable method and low cost.	Difficult to handle because enzyme are PH and Temperature sensitive.
	Microbial Activity	Simple and Naturally occurring process. (e.g.: Leaching)	Show low result as compared to other biological method.

4. Conclusion

There are diverse physical, industrial, and natural strategies existing for the fertilizer immobilization, for example, adsorption strategy, exemplification technique, bio-based epoxy covered urea technique, starch-based superabsorbent polymer, graphene oxide technique, enzymatic technique, and microbial strategy. All strategies have distinctive applications since all these strategies can't relevant for all smaller scale and macronutrient, so a unique strategy is used to immobilize the constituent, for instance, graphene technique is used for phosphorus and give considerably more efficient results when compared to the rest of other strategies. Organic strategy is likewise used, yet condition for response is kept up so troublesome like pH and temperature, so natural techniques are used in this case. Natural burdens become a noteworthy issue and profitability diminishes at an amazing rate. Our trust in synthetic fertilizers and pesticides fortifies but synthetic compounds are hazardous for human utilization as well as for environment. However, fertilizer immobilization can help take care of the issue of sustaining an expansion of the worldwide population when horticulture is confronting different natural anxieties. It is imperative to comprehend the useful parts of immobilization and execute their applications in present day horticultural practices. The new innovation worked with the incredible assets of atomic Biotechnology can upgrade the natural pathways of phytohormone creation. When distinguished and exchanged to valuable fertilizer, immobilization of fertilizer, these advancements can help give alleviation from natural burdens.

Acknowledgement

The authors gratefully acknowledge the efforts of Prof. Bashar Saad from Arab American University for help in making this review article look better with his scholarly suggestion.

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