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Silica nanoparticles: Its green synthesis and importance in agriculture

Sikha Snehal and Pushpa Lohani

Abstract

The only way to increase the crop production with limited land and water resources is by increasing the resource use efficiency along with minimum damage to the soil and environment. The new and emerging branch of science ie., Nanotechnology has the potential to act as an alternative for the conventional agriculture system and thus can be a cure for the major problems faced by agriculture in present times. The use Nano-fertilizers which have many advantages over the conventional fertilizers can be seen as the new idea for improving the quality of the agricultural system. For the plant growth and development, silicon is not considered as essential nutrient; but it is one of the four beneficial elements. It is very important for the plants under biotic and abiotic stress conditions. Reckoning with this fact this review summarizes the process of the green synthesis of Silica nanoparticles, its utility in agricultural perspectives and its storage. This paper also provides the appropriate elucidation of physiochemical and biological approach of silicon nanoparticles in plant that leads to better growth in plant with safe and eco-friendly agriculture.

Keywords: nano-fertilizers, green synthesis, silica nano-fertilizers, nanoparticles storage

Introduction

Due to the “population explosion” in today’s world, the load on increasing the crop production to satisfy the needs of the ever increasing population has also increased drastically over the past few decades. To prevent the humankind from the agony of low food production, intensive agriculture is mainly practiced all round world. Large scale application of fertilizer, herbicides and pesticides is done in order to get more production per unit area. A heavy use of chemical fertilizer culminates in severe environmental issue in agriculture. Out of the total synthetic fertilizers applied, only half is utilized by the plants and the major portion of these chemical fertilizers are leached down the soil. This contributes to pollution of the ground water and the nearby water bodies. The effect of synthetic fertilizers on one hand increases the crop productivity and on the hand it cause soil mineral imbalance and reduces the soil fertility. The recent widespread application of the synthetic chemicals has led to the irreversible changes in the soil structure, soil microbial flora, minerals cycles and even on the food chains leading to drastic effects on the future consumers. In the recent scenario disease and land degradation are two of the major concerns in agriculture

In order to overcome the problems associated with agriculture, an important approach is to develop some alternative that has the property of systemic and targeted release of the chemicals for plants in improving the mineral deficiencies and other growth and development parameters. One way in which this can be done is by use of nanotechnology. Nanotechnology has emerged as one of the leading fields of the science having tremendous application in diverse disciplines including biotechnology and agriculture, this is mainly due to the physiochemical properties of nanoparticles such as the large surface area to volume ratio of nanoparticles (NPs) which provides an enormous reactive interface between the particle and its local environment. For sustainable development, application of biosynthesized nanoparticles can be done in the agriculture field. They can be used for site directed delivery of different nutrients needed for increase in growth, development as well as productivity of plants. The nanoparticles are added at low levels as compared to the chemical fertilizers. The refined use of nanoparticle also reduces the harmful effect of synthetic fertilizers on the environment. Nanoparticles also play an importance role in the protection of plant from diseases, pests and pathogens. The nanoparticles can also affect the modification of the plant gene expression, which in turn results in the changes in the biological and metabolic pathways controlled by the associated genes, and thus affects the plants growth and development.

Silicon has much importance in the life cycle of plants. On the earth, it is the second most abundant element after oxygen, and it is differentially distributed. Fertilizers having silicon is gaining importance in agriculture due to its beneficial effects on the plant growth and development. Silicon has an important role in preventing the plant from biotic and abiotic stress tolerance, because in some crops (rice and horsetail) the absence of silicon increases the susceptibility to fungal pathogens [1]. It also increases plant vigor and resistance to various diseases [2]. Silicon is mainly absorbed by the plants roots in the form of silicic acid through the aquaporin type channel (nod26-like intrinsic proteins and NPs) [3, 4, 5]. Based on the amount of biogenic silica present in their tissues the plants are classified into 3 groups: accumulators, excluders and intermediate type. Rice is the example of accumulators, tomato under excluders and *Urtica dioica* are the intermediate types [6, 7].

Nano-fertilizer versus conventional fertilizers

The word “Nanotechnology” is derived from the Greek word “Nano” which means ”dwarf” meaning one billionth part of a meter. “Nano” means one-billionth, thus nanotechnology refers to materials that are measured in a billionth of a meter. A nanometer is 1/80,000 the diameter of a human hair or approximately ten hydrogen atoms wide. For a particle to be considered as nanoparticle the dimension must be less than 100nm [8]. The surface area to volume ratio of nanoparticles is very high. The unique properties of nanoparticles make it highly applicable to agriculture research, which in turn can help in solving numerous agricultural problems.

Nanotechnology is a very new and interesting field of science and its application are emerging in many areas. Nanotechnology has the ability to make useful changes on various agricultural, environmental, and forestry challenges. Nanoparticles (NPs) are commonly accepted as material with at least 2 dimensions between 1-100 nm [9]. The nanoparticles have some unique properties such as their huge surface area because of which it dominates the contributions made by the small amount of the material, that are different from their molecular and bulk counter parts because they come in the transition zone between the individual molecules and the bulk counterpart [10]. Nanoparticles that are below the size of 20–30 nm are characterized by possessing excess of energy at the surface which is thermodynamically unstable because of the interfacial tension, which acts as a driving force. This leads to a spontaneous reduction of the surface area. Nanoparticles have very high surface energy and very large specific surface area. The use of Nano enhanced solution can increase the seed germination rates, plant protection, growth and development and this is mainly possible due to the judicious or controlled release of the agrochemicals thus reducing the nutrients losses due to leaching, volatilization and other processes.

In the present agricultural system conventional fertilizers are mainly used in order to meet the nutritional requirement of the crop plants. Spraying and broadcasting are the major processes by which conventional fertilizers are applied in the agricultural field. But the final concentration that is reaching to the plants decides the mode of application of the conventional fertilizers. Out of the total concentration or amount of conventional fertilizers applied the concentration that reaches to the targeted site in the plants is very less than the desired concentration. The losses of the conventional fertilizers are mainly due to the runoff, leaching, evaporation, drift, hydrolysis by the water present in the soil, microbial and photolytic degradation. The estimated data of the fertilizer loss after application are as follows; 80-90% of phosphorus, 40-70% of nitrogen, and 50-90% of potassium content is lost in the surrounding environment and are not able to reach the plants due to which there is economic losses as much larger amount of fertilizers are applied than the amount needed by the plants for their growth and development [11, 12]. In order to fulfill the nutritional requirement of the plants there is a repeated application of fertilizers which in the long run adversely affect the nutritional balance of the soil thus causing imbalance in the soil mineral content and the related mineral cycle. There was drastic increase in the fertilizers application rates in 2009-2010 and 2010- 2011 with growth rates of about 5-6% in both [13]. Due to the indiscriminate and injudicious use of the conventional fertilizers has resulted in environmental pollution which in turn affects natural flora and fauna. Due to increased use of fertilizers there is loss in the soil natural flora and reduction in the nitrogen fixation capacity. With the increased use of pesticides there is increased chances of pest and pathogen resistance and also results in the bioaccumulation of the pesticides along the food chain and has resulted in the large scale destruction of the bird’s habitat [14]. Thus due to the above mentioned problems it very important to reduce the amount of synthetic fertilizers used in order to fulfill the nutritional requirement of the crops. So other favorable methods must be used for the fertilization process in order to keep the soil and environment safe from pollution as well as reducing the economic losses.

Nano-materials are synthesized with the help of nano-technology so that the small nano scale particles can act as fertilizer carriers which also have the property of controlled release of the chemicals, high nutrient use efficiency and pose very less harm to the environment so these fertilizers can be categorized as smart fertilizers [15]. Nano-fertilizers are of nanometer regime and it carries the nutrient to be delivered to the crops. The Nano-materials are usually encapsulated in a thin protective polymer film or present in form of emulsion [16]. The surface coating present on the fertilizer by the Nano-material have the ability for the slow release of chemical is because the chemical holds the nano-material very strongly due to high surface tension as compared to the conventional surfaces [17]. The major importance of Nano-fertilizer over conventional fertilizers are enhanced nutrient uptake efficiency, site directed delivery of agro-chemicals and reduction in the toxicity of the environment especially water bodies [18]. The bioavailability of the mineral nutrients is also higher as compared to conventional fertilizers. The effective duration for which the chemicals would be available to plant is also longer as compared to the conventional fertilizers. The conventional fertilizers are available only at the time of delivery the remaining is converted into insoluble salts in the soil [19].

Nano fertilizers

Nano fertilizers can be described as nanomaterial which has the ability to supply one or more nutrients to the plants in order to increase their growth and productivity [20]. Use of Nano fertilizers can be said as one of the promising approach to increase the productivity and growth of the plants to overcome the ever increasing food demands. The Nano fertilizers have very high sorption capacity and surface area and release kinetics of the chemical is controlled which results in the targeted sites delivery of the chemicals [21, 22].

Nano fertilizers can be classified as follows

a. **Macronutrients Nano fertilizers**: Macronutrient nanofertilizers chemically comprises of one or more macronutrient elements such as nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), and calcium (Ca), so they are able to supply one or more of these essential elements to plants.

b. **Micronutrients Nano fertilizers**: The micronutrients that are present in the plant include iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), magnesium (Mg), and molybdenum (Mo). Micronutrient nanofertilizer is rich in essential micro-nutrients present in small quantities which can make a remarkable impact on the quantity and quality of yield. They are expected to enhance uptake of the micronutrient/s by plants even in the worst-case scenarios such as in the soil with high pH, low organic matter and coarse texture.
c. **Nutrients augmented Nano fertilizers:** Nutrient augmented nano-fertilizers are defined as the nano-materials, that are loaded with plant nutrient(s), aimed at increasing plant-uptake efficiency of the nutrient(s) and/ or reducing the negative effects of chemical fertilizer application, but in this case the nano-materials themselves do not contain or supply the targeted nutrient(s). An example of this type of nano-fertilizer is nutrient-loaded zeolites

Nutrients can be encapsulated by nanomaterial coated with thin nano scale polymeric film or delivered as nano-emulsions or nanoparticles (NPs) [13]. Nano material enhanced fertilizers may increase plant uptake efficiency of nutrients and /or reduces the adverse impact of the convectional fertilizer application [20]. The leaching and/or leaking losses of the fertilizers into the soil is reduced with the use of nanostructured formulations. The bioavailability of the mineral micronutrients is increased many folds with the use of Nano-sized formulations as the solubility is increased along with the increase in the dispersion of the insoluble nutrients in the soil and there is reduction in the soil fixation and adsorption of the minerals [16].

Abiotic stress tolerance in plant due to silica

The fundamental requirement of the plants for their growth, development and survival are water, energy (light), carbon and mineral nutrients. Abiotic stress can be defined as the condition of the environment that hampers the normal functioning of the plants. This is mainly due to the fluctuations in the climate the sudden increase or decrease in temperature, heavy rainfall leading to floods, or drought conditions on the other hand. The major abiotic stresses are salinity, thermal and heavy metal stress, drought, flood, etc. Although the plants have the ability to adjust themselves in stressful condition though the process of morphological plasticity yet there is reduction in the productivity and yield of the crops below optimum level. The severity of the abiotic stress is determined by the intensity and the duration. It is one of the major problems in agriculture in present day scenario and is prevalent in all parts of the world.

Silicon deprived plants are usually structurally weaker and very much prone to abnormalities related to development, reproduction and growth. Grasses have maximum concentration of silicon. Silicon functions in triggering responses to a number of environmental constraints. The two processes that contribute to abiotic stress resistance are (a) the mechanical and/or physical protection that is provided by the deposited SiO2 and (b) the biochemical response that trigger chances in the different metabolic pathways. In response to the abiotic stresses the plant follows a defense mechanism releasing reactive oxygen species (ROS) which is known to have damaging properties on the structure and on the different organelles and change the normal functioning of the cell due to changes in physiological processes [23].

The function of stomata is also governed by silicon [24] as well as it enhances the conductance through root by the regulation of the aquaporin [25]. Silicon has role in regulation of the transcription of genes that are involved in water transport, as well as the stress related pathways such as ABA dependent and independent regulatory pathway, phenylpropanoid pathways etc [26]. The presence of silica on the leaf epidermis increases the UV tolerance [27] and decreases the damage caused by UVB on the cell membrane [28]. In case of rice it increases the resistance against lodging by strengthening the stems [29], it brings about reduction of leaf heat-load, which provides effective cooling mechanism and thereby improving plant tolerance to high temperatures. It is also important for the plants growing in drought conditions as double layer of silica cuticle is formed below the leaf epidermis which in turn decreases the water loss due to cuticular transpiration [27] as well as increases extraction of water from the deeper layers of soil as silica induces promotion of root elongation [30].

In the soil that is polluted with metal, the bioavailability of toxic element is influenced by silicon. There is an increase in the rhizospheric pH due to the presence of alkaline Si-containing material or soil sodium metasilicates because of which there is a reduction in the availability of the heavy metal concentration in the soil [31]. The soluble silicate present in the soil gets hydrolyzed and produces gelatinous metasilicic acid that have the property to retain the heavy metals [32].

Phenolics such as Catechins and quercertins are secreted by Si-treated plants, these phenolic compound have strong Al-chelating abilities. Aluminium detoxification is done by the formation of hydroxyl-aluminium silicates in the apoplast [33].

In the heavy metal tolerance compartmentation of toxic ion is very important process. Silicon increases the accumulation of the heavy metals in the endodermis therefore it improves heavy metal retention in the roots [34]. In the silicon treated plants there is increase in the Manganese accumulation in the epidermis of the shoots [35] and the leaf trichome [36]. Silicon induces decrease in the cadmium influx. The hemicellulose bound to silicon which is having a net negative charge is mainly the cause for inhibition of uptake of the cadmium leading to the down-regulation of Nramp5 which codes for a transporter that is involved in the cadmium transport [37].

Silicon also have a major role in the alleviation of salt stress it causes inhibition of sodium ion and chloride ion uptake [38]. The increased resistance to salt stress has been found to be due to the enhancement in the level of the enzymes such as superoxide dismutase (SOD) and catalase. The presence of silicon reduces the translocation of the harmful/toxic ion from root to shoot is also decreased [39]. The NaCl toxicity in rice is reduced by blocking the transpiration due to the SiO2 deposition in endodermis and exodermis [40].

Biotic stress tolerance in plants due to silica

Silicon plays an important role in increasing the plant tolerance against pest and diseases. Initially the tolerance against pest and diseases was thought to be the result because of certain physical and mechanical barrier formed due to the deposition of silicon along the cell wall, but the tolerance is mainly due to the interaction between the host and the pathogen associated with the presence of silicon along with a particular defense response in plant [41].

Silicon mainly prevents the signaling molecule and the effector molecule from attaching to their target cell receptors silicon also induce indirect defense mechanism by changing the composition of the Herbivore-Induced-Plant-Volatilities (HIPV). These compounds have the property to attract the parasitoids to the infested rice plants and kill pests **[42]**. The insects become more prone to predation because the phenology of insects life cycle is also lowered by the silicon present in the plants [43, 44].

Deposition of silicon in plants increases the abrasiveness of the plant tissues and results in reduction of the palatability and digesting the plant tissues rich in silicon is by herbivores and arthropods [45]. The increased resistance in sugarcane against *Eldana saccharina* is mainly due to the silicon deposition [46]. The rate of infection due to the *Rhizoctonia solani* or *Bipolaris oryzae* is decreased as a result of physical strength of the leaf due to Silicon deposition [47, 48].

Presence of silicon increases the resistance against biotic stress by inducing the production of defensive compounds such as phenolics, momilactones and phtyoalexins by the biochemical/molecular pathways [49]. Silicon also results in the activation of certain defensive enzymes like peroxidases, lipoxygenase, polyphenol oxidase and phenylalanine ammonia lyase Silicon increases transcripts level of various defense related genes [50].

Effects of silicon on plants hormones

Silicon has major effect on endogenous phytohormones. The changes in the endogenous phytohormones are mainly observed during the stress condition. During the abiotic stress of high concentration of heavy metal in the soil, the rice plants having high silicon shows a very low concentration of salicylic acid (SA) and jasmonic acid (JA) but the concentration of abscisic acid (ABA) first increase and then after 14 days the concentration of ABA decreases **[51]**. Presence of ABA is related to abiotic stress tolerance specifically drought tolerance. The biosynthesis of ABA has antagonistic effect with JA/SA. Silicon reduces the concentration of JA as a result of wounding [52]. In plants having high silicon content there is an increase in the concentration of gibberellin acid in response to salinity [53].

Resistance against necrotrophic pathogen is mainly associated with ethylene (ET) and JA whereas SA is associated with resistance against bio trophic pathogens. When the plants are exposed to *Erysiphe cichoracearum,* silicon induce increased biosynthesis of the phytohormones such as JA, ET and SA in the leaves [54]. The ET and JA biosynthesis signaling pathways increases in the silicon treated tomato plants which were exposed *to R. solanacearum*, the ET and JA thus increases the resistance against the pathogen [55].

With the treatment of silicon there was an increase in the ET biosynthesis signaling pathway. In sorghum and Arabidopsis silicon increases the biosynthesis of the cytokines which in turn delays senescence [56]. Thus the changes in the plant hormones results in various modifications in the interaction of the hormones with the different physiological and biochemical pathways which results in numerous effects on the plant system.

The distribution of silica in plants

Silicon is mainly stored in the epidermal layer cells in the leaves, in the outer epidermal cells of the inflorescence bracts and the endodermis of the roots. The storage and deposition of silicon in the plants is not a random process but well regulated. There are 3 modes of silicon deposition:

a. Directed paramural silicification of silica cells.
b. Spontaneous cell wall silicification.
c. Directed cell wall silicification.

There are many reports indicating studies carried out to understand the deposition of silicon in the roots and the aerial vegetative tissues, while silicon deposition studies in the seeds are very rare. An observable correlation between the silicon deposition and other elements like N, P, K, S, Mg, Ca, Cl, Zn and Fe was found as a result of ionomics studies. Silicon accumulation was not found in the scutellum or the endosperm. Silicon mainly accumulated in the embryo and the pericarp.

Uptake, translocation and accumulation of nanoparticles in the plants

The uptake of the nano-particles in the plants depends on various factors such as age of the plants, the growing environment as well as the species of the plants. The uptake, translocation and accumulation of nanoparticles also depend on the physiochemical properties of the nano-particles such as size, shape, chemical composition and stability of the nanoparticles in solution [57]. The transporter present in the plasma membrane of the roots of the plants regulates the uptake of the mineral and nutrients.

In many cases the nanoparticles binds to the carrier proteins and pass though the ions channels, aquaporin or by endocytosis. There is a relation between the water and ion uptake by the water (aquaporin) and mineral transporters respectively. Silicon is absorbed by the plants, in the silicic acid [Si(OH)4] form [3, 4, 5]. The silicic acid gets the entry in the plants system mainly by diffusion ie. the apoplastic pathway; but for the entry into the sympast, specific aquaporins (NIP2) is required. The silicic acid gets transported to the aerial tissue through xylem.

The pore diameter of the cell wall (5-20nm) decides the entry of the nanoparticles through it [58]. Thus the size of the nanoparticles or the aggregate of nanoparticles must be less than the pore diameter of the cell so that it could easily pass through the cell wall and reach the cell membrane [59]. The nanoparticles forms complexes with the root exudates or membrane transporters and as a result it can be transported into the plants. In many cases the nanoparticles can also enter the plants through base of trichome in leaf or the stomata.

Once the nanoparticles have entered the cell membrane, they can be transported by either sympastic or apoplastic methods. The nano-particles can be transported from one cell to another by the help of plasmodesmata [57].

Green synthesis of silicon nanoparticles

Considering the immense importance of silica nanoparticles in agriculture, its green synthesis and frequent use in agricultural field is the need of the house. Waste management is usually one of the most complex and cost-intensive public services, even when it is well organised. Nanotechnology is an effective tool in the field of productive science, which helps in the utilization of agricultural food waste into bio energy for human welfare. Energy recovery from waste can play a role in minimizing the impact of agricultural waste on the environment with the additional benefit of providing source for the synthesis of nanoparticles. As most of the common crystalline SiO_2 particles are not in the nanometer-size region, given below are the various processes for the green synthesis of amorphous silica nanoparticles (aSNPs). It is an advantage that silica nanoparticles can be produced from agricultural waste.

A. Green synthesis of silicon nanoparticles using bamboo

Bambo belongs to subfamily of tall treelike grasses of Bambusoideae, the family Poaceae, which comprises of more than 115 genera and 1,400 species. Bamboos have hollow wood like stem which is divided in nodes or joints. It is a very fast-growing, versatile, non-timber forest product whose rate of biomass generation is unsurpassed by any other plants. Its annual increase in biomass is 10-30 % as compared to 2-5 % for trees. Therefore bamboo creates greater yields of raw material for use.

For the synthesis of silicon nanoparticles from bamboo, the bamboo culms were harvested, then the culms were chopped into very small pieces (5mm) using a very sharp razor. For the synthesis only the inner portion of the bamboo stem was used, the outer covering of the culm was removed. The chopped bamboo pieces was then subjected to pyrolysis at high temperature (1250˚C).The pyrolysis was carried out in presence of argon gas at high temperature where the bamboo undergoes self-thermochemical decomposition. During this process there were irreversible changes in the physical state as well as the chemical composition. The pyrolysis is carried out at 1250°C temperature for 12 hours in argon atmosphere in order to remove some of the organic compounds and water from the fresh bamboo pieces this result in the formation of charcoal bio-templates. In order to keep the thermal stress to a minimum the rate at which the temperature was increased was 5˚C/min. The charcoal bio-template was then cooled to 200°C naturally and then it was removed after shutting off the inert atmosphere created by argon. Thus in this way silicon nanoparticles was produced [59].

B. Green synthesis of silicon nanoparticles using rice husk

The rice husk, also known as rice hull, is the outer covering on a seed or grain of rice. It is formed from hard materials; including silica and lignin, the presence of these compounds protect the seed during the growing season. Approximately 600 million tons of rice crops are produced all around the world every year. After milling each kg of rice results in roughly 0.28 kg of rice husk as a by-product of rice production during milling. 20% of the rice plant accounts for the husk, therefore the production of rice husk turn out to be approximately 120 million tons silica comprises about 60% of rice husk [60]. Rice husk as such is considered as an agricultural waste material from the rice milling process and it is usually eliminated by dumping and/or burning. Burning of rice husk is the most economical method for the disposal but this practice generates smoke, as well as breathable dust that contains crystalline silica and other health hazard substances, causing worldwide environmental and health problems. Rice husk can easily be collected from rice mills and can be utilized in synthesis of silica nanoparticles. Silica nanoparticles can be produced using various mathods.

Method 1

The rice husk contains about 60% silica. So to extract the silica from the rice husk, it was boiled for 2 hrs in 10 wt % HCl, then it was washed using deionized water and then the rice husk was dried at 100˚C for 1 day. Now, using the muffle furnace the rice husks were pyrolysed. In order to prepare the silica nanoparticles the muffle furnace was already preheated at 700°C, for 2hrs. The silica nanoparticles produced through pyrolysis was then ultrasonicated in KNO3 at concentration 0.20M, and it was coupled with 1hr of stirring. This was then filtered and dried at 105°C for 4hrs. The filtered and dried sample was pyrolysed at 800°C for 4 hrs which results in semi crystalline porous silica nanoparticle [61]. Fig.1

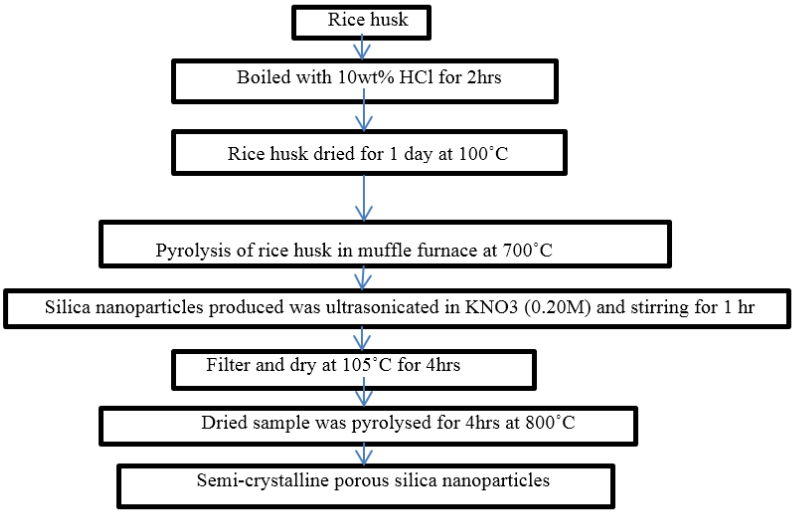

Fig 1: Flowchart showing method for preparation of silica nanoparticles from rice husk.

Method 2

In the following method rice husk was rinsed with deionized water several times in order to remove the dust and then dried overnight in the oven at temperature 90°C. The clean and dried rice husk was gronded into powder, using a countertop before the treatment of ionic liquid, to increase the rice husks surface area. The powdered rice husk was mixed with ionic liquid that resulted in the extraction of lignocellulose. The weight ratio of ionic liquid to rice husk was15:1 [62]. This solution was stirred using a magnetic stirrer and heated in the oil bath at 100˚C for 12 hrs. It resulted in the dissolution of the products, this dissolved mixture was then centrifuged in order to separate any insoluble particles of rice husk. The supernatant was collected and to it deionized water was added, resulting in the precipitation of the dissolved lignocellulose. The precipitated lignocellulose was collected and washed with deionized water, and dried overnight at 90˚C. The dried lignocellulose was pyrolysed for 2hrs at 700˚C in order to produce silica nanoparticles. Fig.2

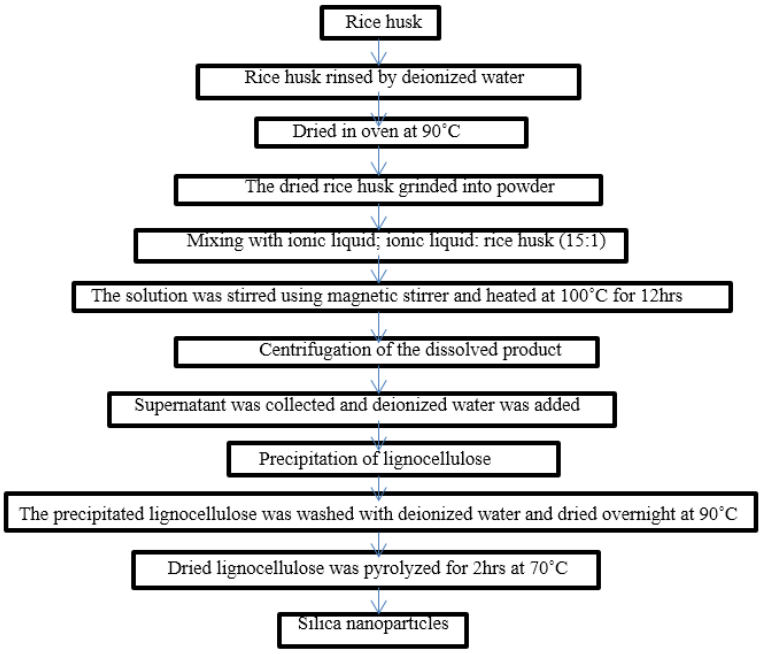

Fig 2: Flowchart showing procedure for the preparation of silica nanoparticles from rice husk (lignocellulose)

Method 3

In the following method rice husk ash was used. The primary components of rice husk ash are hemicellulose, cellulose, lignin and silica. The organic composition was decomposed after burning resulting in the formation of the rice husk ash [63, 64, 65]. Rice husk ash is a very rich source of silica, as it contains 90-98% of silica along with some metallic impurities [66, 67, 68, 69, 70]. The silica present in rice husk ash has very large surface area and it is mainly in the amorphous state [71, 72].

The rice husk was pretreated with acid and heat. The rice husk was treated using 30 wt% sulfuric acid and 10% hydrochloric acid solutions. After this the material was kept in muffle furnace at 600˚C for a period of 4 hours in order to get rid of the entire hydrocarbon which was incorporated in it. The acid washing step was important for removing the mineral impurities. Acid leaching of the rice husk ash was done with 10% HCl followed by addition of 30 wt% sulfuric acid solution was added at a temperature of 100˚C. The mixture was kept for 2 hours in pyrex three-neck round bottom flask that had a reflux condenser in the hemispherical heating mantle. The slurry obtained after the above process was filtered and washed with the help of distilled water many times till the pH value of 7 was achieved [73]. Fig.3.

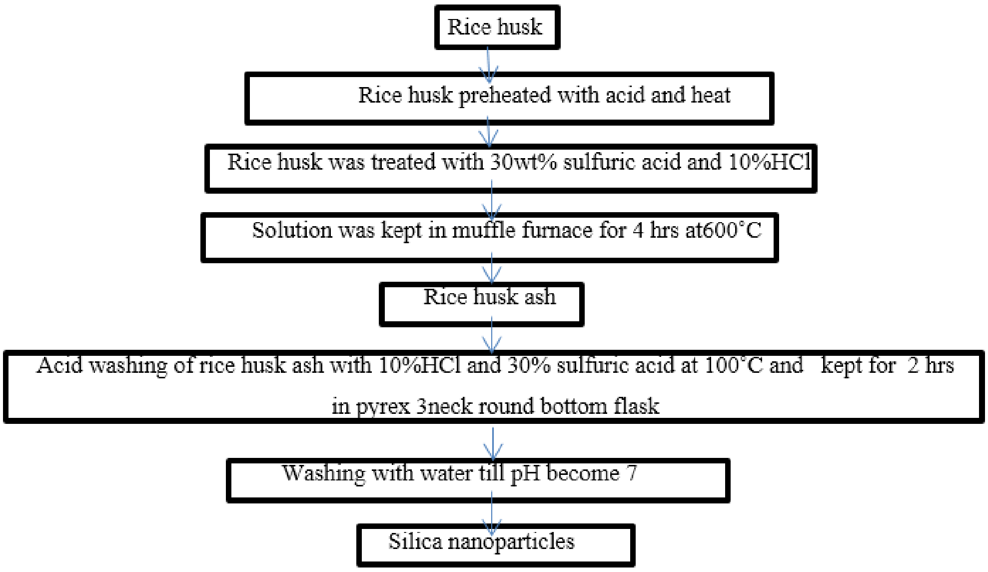

Fig 3: Flowchart showing the method for the preparation of silica nanoparticles from rice husk ash

C. Green synthesis of silica nanoparticles using sugar beet bagasse

In order to obtain sugar beet bagasse ash, the sugar beet bagasse was calcinated at 500°C for a period of 12 hours. After that 1 g of sugar beet bagasse ash was taken and then treated with concentrated HCl:HNO_3= 1:3 (v/v) at 35°C for 2 hours and then dried in the oven at 60°C. The residue was obtained and to this 50ml water was added. Concentrated NaOH was added to make the solution alkaline (pH 13-14). The solution was kept overnight now the alkaline solution was neutralized using HCl. The sample was then filtered with the help of a 0.22μm filter to remove the fibers from the nanoparticle solution [74]. Fig.4

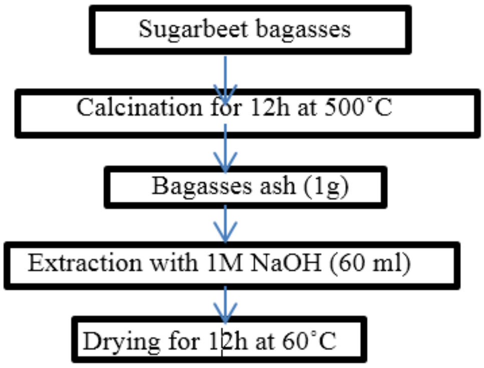

Fig 4: Flow diagram of the process used in the preparation of silica nanoparticles from Sugarbeet bagasses

Storage of silica Nanoparticles

The synthesized silica nanoparticles need to be stored before being utilized. The silica Nanoparticles powders and dispersions are stored at room temperature. They can also be refrigerated if needed. The nanoparticles are stable for 1 year when stored at room temperature. When the Nanoparticles are stored at room temperature for long time, it may settle at the bottom of the vial. The settling of the nanoparticles depends upon the size the larger particles settle much faster than the smaller one. So before using the nanoparticles the vial is vigorously shaken in order to obtain a homogenous solution. This requires only 30sec of mixing. Otherwise bath sonication for a time period of 10 -15minutes is very effective method for re-suspending the nanoparticles that have settled at the bottom of the vial. The bottom of the container must be visually inspected to ensure that no nanoparticles are settled at the bottom. To the storage vial that contains dry silica nanoparticles, water or any appropriate solvent is added. If small amount of nanoparticle is needed then it could be transferred and re-dispersed. One must be careful while handling dry silica nanoparticles as they possess inhalation hazards. 1ml of solvent is added to every 10mg of the nanoparticles and then bath sonication is done for 20-30 minutes or until the complete dissolving of the particles takes place. For re-dispersing low pH buffer (4-5) such as ethanol or acetate is used.

Silica nanoparticles delivery system

Silica nanoparticles can be delivered to the plants in many ways. These include invitro and invivo method

In vitro methods

a) **Hydroponics*:*** The method of hydroponics was 1st used by Gericke (1937) mainly for dissolving inorganic salts. The method is also known as “solution culture”. In this method the plants are grown in absence of soil with their roots immersed in the nutrient solution. The pH, concentration of nutrients in the solution as well as the oxygen demand of the solution is maintained regularly. The old nutrient solution is removed from one end and new nutrient solution is added from the other. The required concentration of silica nanoparticles are mixed in the hydroponics system. The powered silica nanoparticles are weighed and then added to the solution, the concentration can vary in the range of 25mg/L, 50mg/L, 75mg/L or 100mg/L depending upon the requirement of the study. The only disadvantage of this method is the attack of pathogens and wilting which is caused due to the high moisture rates.

b) **Aeroponics:**_The method of aeroponics was 1st used by Weathers and Zobel (1992). In this method the plants are grown in absence of sol, the roots are suspended in air and the solution containing the nutrients are sprayed on to the roots continuously. The gaseous environment around the roots is controlled. The silica nanoparticles are prepared in ppm concentration as the solution is to be sprayed on the roots of the plants. The concentration in ppm may vary according to the requirement of the plants as well as the experiments. Use of aeroponics is rare because high level of nutrients is required to be sprayed in order to sustain the growth of the plants.

In vivo methods

a) **Soil application:** Nutrient application though soil application is the most common method to provide nutrients to the plants. The major factors to be kept in mind while applying the nanoparticles though soil application are the texture of the soil, salt content of the soil, pH of the soil, soil texture, and how long will the nanoparticles will be able to release the agrochemicals. The adsorption of the mineral nutrients depends upon the negative soil particles present in the soil. The cation exchange capacity of most of the agricultural soil is larger than the anion exchange capacity [75]. The application of silica nanoparticles in soil is the most widely used method, as the solution of the silica nanoparticles is made and it is directly applied to the soil. According to the water requirement of the plants and the type of soil, silica nanoparticles concentration varies. The most commonly used concentration is 25mg/L, 50mg/L, 100mg/L

b) **Foliar application:** this is a method where the liquid silica nanoparticles are directly sprayed on the leaves of the plants. This is an efficient method for the application of mineral nutrients as it decreases the time period between the application and uptake of the nutrients by the plants generally when the plants are in rapid growing phase [75]. When used for nanoparticles foliar application has an upper hand as the stomata and leaf epidermal cell are mainly involved in the uptake of the nanoparticles. The spraying is mainly done during morning and evening because the opening of stomata is maximum during these time. The solution is prepared in distilled water in different concentration such as 200ppm, 250ppm, 300ppm, 400ppm and 500ppm, a particular concentration is selected for spraying on the leaves for the particular set up of an experiment. The solution is sprayed on the leaves with the help of sprayer.

Success stories of silica nano-particles

Mesoporous Silica Nano particles (MSNPs) usually 20nm in size are generally used. The MSNPs is taken up by the root system through the apoplastic and symplastic pathways and is translocated to the aerial parts of the plants through the xylem system [76]. MSNPs are mainly deposited in the cell walls, so they have very high with the other cell wall components. For the efficient uptake of the Nanoparticles there must be a fine tuning between the pH and the surfactant concentration, these two decides the size and nature of the MSNPs, the entry of the MSNPs takes place through the pores present in the cell wall [76].

With the use of MSNPs the total protein content increased, the growth was boosted; the photosynthesis of lupin and wheat seedlings increased but there were no changes in the antioxidant enzyme activity [77]. The shift of 14/cm and 10/cm in the Raman peak of chlorophyll was observed in wheat and lupin, this suggested that there was a change in the chlorophyll structure [77].

In tomato which comes under the category of silica excluders, the application of silica Nanoparticles resulted in increased germination of the tomato seeds. The SNPs was applied at the concentration of 8g/L along with the increase in the germination rate of tomato seedlings there was also an increase in the fresh weight and the dry weight by 1116.6% and 117.5% respectively [78].

Silica Nanoparticles were observed to stimulate the antioxidant defense system in order to protect the wheat seedling against the UV-B abiotic stress [79]. The SNPs decreased the damage caused by the UV-B stress such as tissue damage, low fresh weight and decreased chlorophyll content. The protective roles through the modification of the NO levels were observed as the nitic oxide attained a peak after SNPs+UV-B treatments. When the Nanostructured SiO2 (TMS) was applied to the roots of 1 year old larch seedlings by soaking for 6h, the results showed promotion in the chlorophyll content, lateral root growth, and main root length [80].

The application of low concentrations of silica nanoparticles have shown to improve seed germination rate of tomato [78]. According to [81] Silica nanoparticles application has increased seed germination in maize seeds as it helps in providing better nutrients uptake, the pH and conductivity of the growing medium was also maintained by its use [80]. The exogenous application of silica nanoparticles on Changbai larch (*Larix olgensis*) seedlings showed that nano-SiO2 has a role in improving seedling growth and quality, including the mean height, the diameter of the root collar, the number of lateral root and the main root length of seedlings and also geared up the process of synthesis of chlorophyll. In tomato silica nanoparticles application augments seed germination under abiotic stress [82].

In squash application of silica nanoparticles enhanced rate of seed germination and also stimulated the effect of antioxidant system under salinity stress [83]. Exogenous application of silica nanoparticles resulted in the improvement of the seed germination rate of soybean by increasing the concentration of nitrate reductase [84] and also by enhancing ability of the seeds to absorb and utilize nutrients and water [85]. Under salinity stress conditions, the application of silica nanoparticles has shown to increase the leaves fresh and dry weight, chlorophyll content and proline accumulation in plants.

The tolerance of plants to endure abiotic stress has increased with the increase in the accumulation of free proline, free amino acids content, antioxidant enzymes activity as a result of application of silica nanoparticles [86, 87, 82, 83]. The application of silica nanoparticles have shown to increase the plant growth and development by enhancing the gas exchange via stomata and chlorophyll fluorescence parameters, which are as follows net photosynthetic rate, stomatal conductance for gas exchange, transpiration rate, potential activity of PSII, actual photochemical efficiency, electron transport rate, effective photochemical efficiency and photochemical quench [83, 88].

Conclusion

Nanotechnology is definitely an evolutionary science and has introduced many novel applications in the field of agricultural science. The extensive use of the agrochemicals in order to increase the crop productivity has already polluted the ground water, top fertile soil and even its increased concentration in the food. So increasing the productivity is important but the damage to the environment should also be minimized, this problem can be solved by the use of nanotechnology. Plants can very efficiently utilize the nutrient-containing nanoparticles as a source of essential mineral with the help of their roots or leaves, thus maintaining or enhancing their metabolism, growth, anti-pathogen capacity and yield. As emphasized in the introductory part of the review the nano-fertilizers plays important role in increasing the food production. It also minimizes environmental disruption which is caused due to the excessive use of agrochemicals. Silica is very abundant on earth and as discussed above there are numerous positive effects on the plants which in turn makes it very important element in agriculture. The silica nanoparticles can lead to better performance as compared to the conventional fertilizers. The silica nanoparticles increase the biotic and abiotic stress tolerance in plants. The synthesis of nanoparticles from different waste materials such as rice husk and sugar beet bagasse can serve the purpose of waste management, by recycling. The storage of silica nanoparticles is very simple as it can be stored at room temperature or - 4˚c. There are many examples cited above in order to proof the success of silica nanoparticles.

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