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PLANT BIOSTIMULANTS BASED ON NANOFORMULATED BIOSILICA RECOVERED FROM SILICA-RICH BIOMASS

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Abstract

This review evaluates the technological solutions used to produce nanoformulated plant biostimulants made from biosilica recovered from silicon-rich biomass. Silicon improves root nutrient uptake/nutrient use efficiency, increases plant tolerance to stress, and promotes phytonutrients in edible crop yield. The exact mechanism of silicon action is not yet known. However, it is generally accepted that a flow of soluble silicon species through plant simplast is essential to produce the aforementioned effects. The main difficulties in applying soluble silicon species, silicic acid, and its di- and trimers to plants are related to the polycondensation features at very low concentrations. One of the solutions to this technical problem is to use amorphous silica, which constantly releases small quantities of soluble silicon species. For example, phytoliths formed in several plant species that concentrate the simplast flow of soluble silicon in their simplast are an excellent source of soluble silicon. Nanoformulation increases the surface/volume ratio and further improves the release of soluble silicon species. Our review focuses on the techniques used to extract and nanoformulate the biosilica from silicon-rich biomass.

Key words: *biosilica, nanoformulation, plant biostimulant, soluble silicon.*

INTRODUCTION

Bionanoparticles and biomass-derived nanoformulations are spreading in agriculture and plant-related applications due to their remarkable physical-chemical particularities such as size, shape, specific surface area, multi-functionality, biochemical activity, and stability, aiming to enhance yield and crop quality in a sustainable, circular paradigm.

Silicon (Si) is not considered a nutrient for plants but mainly a microelement with beneficial effects (Constantinescu-Aruxandei *et al.*, 2020). It is known that Si has two main functions in plants: a structural one, associated mainly with Si translocated by apoplast, and a physiological one, usually associated with soluble Si translocated by simplest (Casey *et al.*, 2003).

Soluble silicon was classified as an inorganic plant biostimulant (Savvas & Ntatsi, 2015). Plant biostimulants represent a new category of agricultural inputs, and their production from plant extracts is a sustainable approach to valorize the side streams (du Jardin, 2015). Recent studies and debates have led to the conclusion that "*A plant biostimulant shall be an EU fertilizing product, the function of which is to stimulate plant nutrition processes independently of the product's nutrient content with the sole aim of improving one or more of the following characteristics of the plant or the plant rhizosphere: i) nutrient use efficiency, ii) tolerance to abiotic stress, iii) quality traits, or iv) availability of confined nutrients in the soil or rhizosphere*", as stated in the European Regulation 2019/1009 (Regulation, 2019).

Although plants have the ability to regulate their functions under stress, there is a reduction in crop and yield productivity below an optimal level of the parameters that play a vital role in plant development (Fahad *et al.*, 2017). Silicon-free plants are structurally weaker and highly prone to developmental, reproductive, and growth changes because Si acts as a trigger for plant protection mechanisms against biotic and abiotic stress. Therefore, in terms of plant resistance to abiotic stress, two major factors are thought to be involved (a) the mechanical and/or physical protection provided by deposited amorphous silica, respectively (b) the biochemical response that triggers different metabolic pathways (Etesami & Jeong, 2018).

SILICON IN PLANTS

Even if all terrestrial plants have silicon (Si) in their tissues, the concentration varies according to species, ranging from 0.1 to 10% Si in dry weight (Epstein, 1994; Ma *et al.*, 2007). This difference in silicon accumulation between plant species has been attributed to the specificity of roots to take up silicon. Thus, three ways in which Si can be accumulated by higher plants in relation to water uptake have been proposed: active uptake (the Si uptake rate is much higher than the water uptake), passive uptake (soluble silicon and water are taken up similarly in terms of uptake rate) and partial rejection (water uptake rate is higher than that of soluble silicon) (Carey & Fulweiler, 2014; Ma *et al.*, 2007). Plants that accumulate a high amount of silicon include horsetail (*Equisetaceae* family) and rice, corn, or wheat (*Poaceae* family) species. Other plant species, such as nettle (*Urticaceae* family), accumulate a relatively moderate amount (Luyckx *et al.*, 2017).

The available soluble in soil largely depends on biosilica recycling (Schaller *et al.*, 2021). The available silicon in soil refers to the amount of silicon that the growing plants can take up during the growing season. The liquid phase (soil solution) contains soluble silicon, i.e., orthosilicic acid (H_4SiO_4) and its di- and trimers, the only silicon molecular species that plants take up. Orthosilicic acid, H_4SiO_4, is taken up from the soil solution at concentrations between 0.2 and 0.6 mM (Epstein, 1994). Orthosilicic acid is a very weak acid with four acid functions and with the lowest pKa value of 9.8. This means that at pH 9.8, orthosilicic acid is present in the undissociated state in a proportion of 50% and 50% of it in the dissociated state. Between pH 2 and 8, orthosilicic acid is a neutral, completely non-dissociated molecule. At concentrations higher than 2 mM, it starts to polymerize through polycondensation reactions with the release of water (Spinde *et al.*, 2011). The main factors that influence the bioavailability of silicon in soil are the soil type, pH, texture, temperature, organic matter, or the ions present in the soil (Kawaguchi & Kyūma, 1977). In the soil, silicon is an element with reduced mobility (Cornelis & Delvaux, 2016). Soluble silicon species, formed by weathering of the silicate rocks, are precipitated by the co-released aluminum ions and generate clays (de Tombeur *et al.*, 2021).

In the last decade, different silicon transporters have been discovered in the plant tissues of several species. The flux of soluble silica, i.e., H_4SiO_4, and the species resulting from its dimerization/trimerization, taken up from the soil by the roots and passing through the symplasts, causes balanced priming of the different defense pathways in the plants (Van Bockhaven *et al.*, 2013). Once in the symplast via the *Lsi1* transporter, Si is transferred to the apoplast via the *Lsi2* transporter and further via the transpiration process. Si reaches the xylem as monosilicic acid (Casey *et al.*, 2003). Subsequently, in the metabolic active plant tissues, by the concentration of silicic acid due to water loss by evaporation, silicic acid polymerizes to amorphous silica [$(SiO_2)_n$ x nH_2O], known as opal or phytolith. The resulted amorphous biosilica is deposited in specific cells. In some species, removal of Si from the xylem is also an active, transporter-mediated process. *Lsi6* is thought to be involved in the translocation of Si from the xylem, a transporter identified in the *Poaceae* family (Ma & Yamaji, 2015; Mitani-Ueno & Ma, 2021).

In plants, silicon is stored in a solid form defined by phytoliths which are micrometer-sized amorphous silica structures that protect the plant cell wall against abiotic stress. The cell wall polysaccharides mediate silica deposition and phytolith formation (Nawaz *et al.*, 2019). Silica from the plant cell wall is coupled with lignin polymerization and cell wall oxidative level (Zexer & Elbaum, 2020).

It is known that abiotic stress can take many forms that hinder plant growth and development by slowing down physiological processes, and that can even lead to plant tissue senescence. One of the ways in which silica delays cell senescence and thus strengthens the plant cell wall is by amplifying the synthesis pathway of suberin monomers and monolignols (Fleck *et al.*, 2011). The silicic acid-mediated suberification process slows down the water loss through evapotranspiration and even protects plants against pathogenic microorganisms (Harman-Ware *et al.*, 2021).

Plant exposure to various abiotic and biotic stress conditions also leads to the release of reactive oxygen species (ROS), activating plant defense responses. ROS accumulation determines a cascade of biochemical reactions at the cellular level (Hasanuzzaman *et al.*, 2020). Silicon has the ability to alleviate ROS induced stress in plant cells and tissues in several ways, such as attenuating the lipid peroxidation process of cell membranes, increasing or decreasing the level of endogenous phytohormones (Kim *et al.*, 2014), or activating the antioxidant defense system of plants (Ali & Hassan, 2017; Verma *et al.*, 2021). We summarized in Table 1 some of the effects reported in silicon-treated plants as a response to stress.

Table 1. Response of silicon-treated plants to abiotic and biotic stress

Plant type	Stress	Effect in Si-treated plants compared to untreated plants	References
Rice (*Oryza sativa*)	Heavy metals	Decrease in SA* and JA*; increase in ABA* Decrease in lipid peroxides Increase in plant growth Increase in chlorophyll content	(Kim *et al.*, 2014)
Strawberry (*Fragaria* sp.)	Salt	Increase in chlorophyll content Increase in carotenoid content Increase in plant growth	(Avestan *et al.*, 2019)
Roselle (*Hibiscus sabdariffa* L.)	Drought (water deficit)	Increase in SOD*, CAT*, POD* Increase in plant growth	(Ali *et al.*, 2017)
Sugarcane (*Saccharum officinarum* L.)	Water excess	Increase in SOD, CAT, APx* activity Increase in chlorophyll content Increase in photosynthesis activity	(Verma *et al.*, 2021)
Wheat seedlings (*Triticum aestivum* L.)	UV-B	Increase in antioxidant enzyme activity Increase in chlorophyll, flavonoid, and anthocyanins content Increase in plant growth	(Yao *et al.*, 2011)
Maize (*Zea mays* L.)	Low temperature	Constant level of IAA*, GA*, CKs* Increase in antioxidant enzyme activity	(Moradtalab *et al.*, 2018)
Tomato seeds (*Solanum lycopersicum* L.)	Heat	Activating plant defense mechanisms (increase in antioxidant enzyme activity)	(Khan *et al.*, 2020)
Yellow melon	*Acidovorax citrulli* (bacterial infection)	Protection against bacterial fruit blotch (BFB) Decrease in ABA and SA phytohormones	(Ferreira *et al.*, 2015)
Arabidopsis thaliana	*Erysiphe cichoracearum* (fungal disease)	Stress alleviation	(Fauteux *et al.*, 2006)

*Abbreviations: SA (salicilyc acid), JA (jasmonic acid), SOD (superoxide dismutase), CAT (catalase), POD (peroxidase), APx (ascorbate peroxidase), IAA (auxins), GA (gibberellins)

Soluble silicon modulates the level of various types of plant hormones. According to the effect of phytohormones on plant growth, they are divided into stimulants - auxins (IAA), gibberellins (GA), cytokinins (CKs), salicylic acid (SA), and inhibitors: abscisic acid (ABA), ethylene (ET), jasmonic acid (JA) (El Sabagh *et al.*, 2022). Depending on the stress type, silicon cross-talks with each of these hormones, balancing the stimulation and the inhibition of the tissular and cellular processes (Lesharadevi *et al.*, 2021).

NANOBIOSILICA EXTRACTED FROM SILICON-RICH BIOMASS

As we mentioned, silicates mineral weathering determines the formation of clays (de Tombeur *et al.*, 2021). Hydrated silica nanoparticles, SiO_2 x nH_2O, represent the only form with known efficiency in the released quantities and bioavailability of silicon to the root and further to the plant tissues (Epstein, 1994). The phytoliths accumulated in plants, especially in the silicon-accumulator plants, act as silicon sinks and silicon sources(Cornelis *et al.*, 2016). This section will focus on the recovery of silica nanoparticles from phytoliths, namely chemical extraction and maceration of silica-rich plants, widely used in organic agriculture.

Particular types of biomass wastes were found to be rich in biosilica, such as rice and oat husks, wheat and rice straws, horsetail, corn cobs, sugarcane bagasse, or bamboo and reed (*Phragmites australis*) leaves, with a very high level of biosilica (Athinarayanan *et al.*, 2017; Kow *et al.*, 2016; Schaller *et al.*, 2013; D. Schneider *et al.*, 2020; Vaibhav *et al.*, 2015). From such biosilica-rich biomass, silicon is recovered mainly in the form of nanosilica. The silicon extraction methods can generally be divided into alkaline or acid techniques. Some relevant studies in various extraction conditions are presented in Table 2.

Table 2. Extraction conditions of biosilica from different types of biomass wastes

Biomass type	Extraction conditions	Silica yields and properties	References
Rice husk	Ball milling, 0.2M NaOH, KOH, 80°C, 3 h, 6% w/v, washing, calcination 6 h at 900°C	98.5% Silica, 1.97 m^2/g, SSA, 0.004 cm^3/g, pore-volume, NaOH leads to a higher yield than KOH	(Park *et al.*, 2021)
Rice husk Sugarcane bagasse Groundnut shell Bamboo leaves	Drying, calcination 7 h at 900°C, 1M NaOH to dissolve SiO_2, precipitation 24 h with 6M H_2SO_4	98% SiO_2	(Vaibhav *et al.*, 2015)
Sorghum husk	Drying, 1:5 S/L, 0.1N HCl, 120°C, 15 lbs., drying, calcination 20 min at 600°C	95% Silica, 50-300 μm particle size	(Periasamy *et al.*, 2018)
Horsetail	Drying, 1:10 S/L, 2% H_2S0_4, 140°C, calcination 2h at 650°C	30-50 nm particle size	(Mattos *et al.*, 2018)
Rice Oat Spelt husk Rice husk Horsetail	Drying, 1:13 S/L, water, 24 h, filtration, 1:13 S/L, 3.25M citric acid, 323K, 24 h, filtration, washing, calcination 30-210 min at 583-783K	>90% Silica, 185-303m^2/g SSA, 0.35-0.46 cm^3/g pore volume, 2-30 nm pore size	(Denise Schneider *et al.*, 2020)
Sugarcane bagasse	Crushing, sieving to a size of 0.5-1 cm, 1:6 S/L, 1N HCl, 120°C, 2 h, 15 lbs., washing, drying, calcination at 550°C, 650°C, 750°C	251, 210, 191 average particle size for the nanobiosilica prepared at three different calcination temperature	(Athinarayanan *et al.*, 2017)
Rice husk	1:5 S/L, 1N HCl, 120°C, 2 h, 15 lbs., washing, drying, calcination at 500°C, 600°C, 700°C	10-30 nm particle size, spherical shape,	(Athinarayanan *et al.*, 2015)
Horsetail	Drying, sieving, 1:50 S/L, HCl 4M, 2 h boiling, washing, drying, calcination 2h at 500°C	Mesoporous silica network, 450m^2/g SSA, about 15 nm particle size	(Hosseini Mohtasham & Gholizadeh, 2020)
Sugarcane bagasse Corn cob	Drying, sieving, calcination 400-1000°C, 1:6 S/L, 1N NaOH, 80°C, cooling, 1N HCl to reach neutral pH, desiccation 12 h, 80°C	17.23 nm average crystallite size, nano-agglomerated, irregular shape	(Goswami & Mathur, 2022)

*Abbreviations: S/L = solid/liquid ratio

The extraction processes generally start with a grinding step and end with a calcination step. Mechanical grinding using ball milling or chopping blender is necessary to reduce particle size and increase the surface area for the next leaching step. Alkaline or acidic treatments aim to destruct the lignocellulose matrix by dissolving the soluble fibers, mainly hemicelluloses, and further decrease the particle size for the carbonization/calcination step. By calcination at 400-900°C, the remaining organic phase consisting of cellulose and lignin is decomposed in volatiles, CO_2, and water, leaving behind the inorganic phase predominant in silica. The resulting nano(bio)silica from phytoliths was used to promote plant growth and enhance stress tolerance in cultivated plants (Mathur & Roy, 2020).

Maceration is a process used since ancient times through which bioactive compounds are released from plant material into the extraction solvent. This process has become widespread as a recovery method for compounds with productivity and crop quality enhancing properties. As we already mentioned, there are silica-rich plants due to their capacity to uptake silicon faster than water (Richmond & Sussman, 2003). Such plants were used to manufacture fermented macerates used in organic/biodynamic agriculture (Proctor, 2012). Horsetail is the common name that has been assigned to plant species that belong to the genus *Equisetum*. These plants contain a significant amount of silicon deposited in plant tissues in the form of phytoliths. There are theories that the rich silicon content, i.e., 25% of the dry mass of horsetail species, has replaced the lignin content, which is about 12%. Therefore, silicon plays one of its functions in strengthening the cell wall structure (Yamanaka *et al.*, 2012). Moreover, the potential of *Equisetum arvense* L. in crop protection has been recognized, as stated in the European Regulation No 462/2014 (Regulation, 2014), especially for the ability of silicon to alleviate the stress induced by fungal diseases (García-Gaytán *et al.*, 2019).

Nettle is the common name for plant species belonging to the genus *Urtica* (Đurić *et al.*, 2019; Kregiel *et al.*, 2018), and they have been used for centuries to treat various medical conditions due to their rich content in compounds with antimicrobial (Kregiel *et al.*, 2018), anti-inflammatory (Johnson *et al.*, 2013), antioxidant (Telo *et al.*, 2017) activity. In nettles, the rate of silicon uptake from the soil is similar to that of water uptake, and Si gets deposited even in the stinging nettle (Sowers & Thurston, 1979). Thus, they are considered moderate accumulators of silicon (Luyckx *et al.*, 2017; Sowers *et al.*, 1979). Several studies have been reported in which horsetail or nettle macerates have been used as plant biostimulants or control agents against plant pathogens. We presented some of them in Table 3.

Table 3. Response of macerate-treated plants to different conditions

Plant type	S:L ratio	Maceration time	Final concentration applied	Environment condition	Effect in horse-tail macerate-treated plants compared to untreated plants	References
Horsetail	200 g: dry plant:10L water	Soaking 30 min, boiling 45 min	2 mg/mL	Grapevine trunk diseases (GTDs)	25% inhibition of fungal growth	(Langa-Lomba *et al.*, 2021)
Horsetail	600 g dry leafs:10L water	7 days for Si release	12 kg/hL	Fungal pathogens	Si slowed down the water excess that could lead to fungal growth Increase in crop yield with 30%	(Trebbi *et al.*, 2021)
Nettle	15 g dry leafs:1L water	3-4 days	2 mg/mL	Grapevine trunk diseases (GTDs)	25% inhibition of fungal growth	(Langa-Lomba *et al.*, 2021)
Nettle	183 g dry plant:10L water	24 h / 14 days	Dilution 1:3 ratio	-	Increase in leaf area of green beans Increase in height and stem diameter	(Maričić *et al.*, 2021)

NANOFORMULATED PLANT BIOSTIMULANTS MADE FROM BIOSILICA EXTRACTED FROM SILICON-RICH BIOMASS

Nanoparticles (NPs) are defined as particles with a size between 1 and 100 nm (Khan *et al.*, 2019). The abundance of nanoparticles in plants depends on various factors such as plant age, growth environment, or species (Luyckx *et al.*, 2017; Rajput *et al.*, 2020; D. Tripathi *et al.*, 2016). The uptake rate, translocation, or degree of storage of nanoparticles also depend on the nanoparticles' physicochemical properties, such as size, shape, chemical composition, surface/volume ratio, or nanoparticles stability in solution (Ferdous & Nemmar, 2020). The chemical structure of most silica forms consist of one silicon atom bonded to four oxygen atoms in a tetrahedral unit. Crystalline forms of silica have a regular structure. In contrast, amorphous forms are composed of highly disordered tetrahedral units of silicon and oxygen, bonded randomly, without a defined pattern (Perry, 2009). The polymeric structure of silica nanoparticles consists of siloxane (-Si-O-Si-) groups formed by covalently bonded oxygen and silicon atoms and silanol (Si-OH), highly concentrated at the surface (Zhuravlev, 2000). In addition, depending on the use, silica nanoparticles (SiNPs) can be functionalized with various compounds resulting in multifunctional nanoconjugates.

Nanoparticles uptake into the plant structure depends on the pore diameter of the cell wall (2-20 nm) (Kurczyńska *et al.*, 2021). Thus, the size of the synthesized nanoparticles or nanoparticles aggregate must be smaller than the pore diameter of the cell so they can easily pass through the cell wall and reach the cell membrane (Augustine *et al.*, 2020). As a pathway into plant tissues, silica nanoparticles can form complexes with specific transporters or root exudates (Bhat *et al.*, 2021; de Moraes & Lacava, 2022; Wang *et al.*, 2022). Translocation of nanoparticles through plasmodesmata has also been reported (Kurczyńska *et al.*, 2021).

Plenty of studies support the role of silicon nanoparticles in agriculture due to their remarkable properties - their nanometric size and high mobility through the plant tissues. Some relevant studies are presented in Table 4..

Table 4. Response of SiNPs-treated plants to different conditions

Plant type	SiNPs size	Stress	Effect in SiNPs-treated plants compared to untreated plants	References
Hawthorn berry (*Crataegus* sp.)	10-30 nm	Drought	Increase in plant growth Constant electrolyte leakage index Decrease of MDA Increase in chlorophyll content	(Ashkavand *et al.*, 2015)
E. sativa	17.23 nm	-	Increase plant growth Increase in protein content Increase in chlorophyll level Increase in polyphenol content	(Goswami *et al.*, 2022)
Maize (*Zea mays* L.)	20-40 nm	-	Increase in phenolic compounds	(Suriyaprabha *et al.*, 2014)
Maize (*Zea mays* L.)	20-40 nm	-	Enhance soil nutrient content	(Rangaraj *et al.*)
Lentil (*Lens culinaris* Medik.)	20-30 nm	Salt	Increase in seed germination Stress alleviation Increase in plant weight	(Sabaghnia & Janmohammadi, 2015)
Maize	150-200 nm	Heavy metals	Stress alleviation	(D. K. Tripathi *et al.*, 2016)

*Abbreviations: MDA (malondialdehyde)

Despite many studies demonstrating the silicon plant biostimulant activities, soluble silicon and nanobiosilica produced from plant phytoliths are still not-used routinely in crop production (Zellner *et al.*, 2021). The main reason for such underutilization is presented in Figure 1. Future studies, including those that will reinforce the link between (nano)biosilica and the beneficial effects of macerated plant extracts, will promote silicon utilization by the farmers.

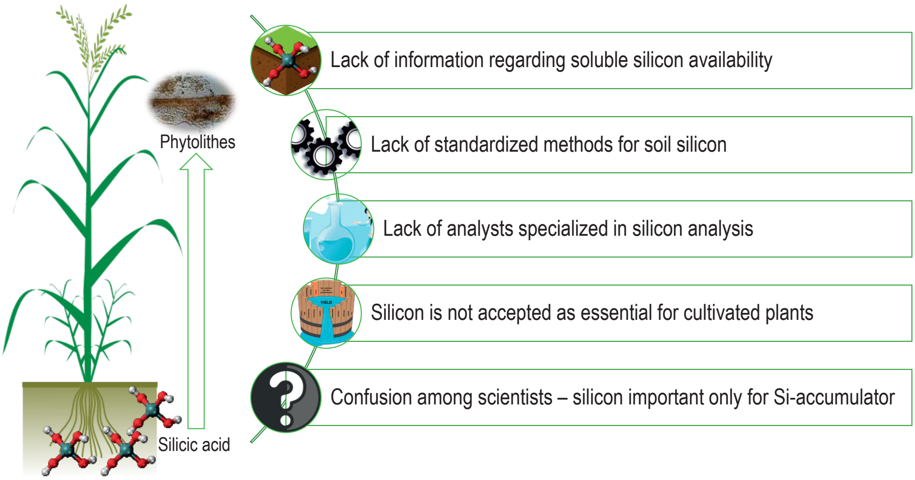

Figure 1. The main reason for the underutilization of silicon in crop management.
Information adapted from Zelnner *et al*., 2021

CONCLUSIONS

Soluble silicon is beneficial for cultivated plants and the proper function of ecosystems. The silicon mode of action is not fully understood. However, the studies reported till now reveal silicon potential in mitigating abiotic stress amplified by climatic changes.

Soluble silicon is still not routinely used in crop management. One direction to increase silicon utilization in agriculture is to accelerate the studies demonstrating (nano)biosilica as one of the main ingredients of macerated plant extracts. Such macerated plant extracts are largely used in practice. The academic community's interest in studying such macerated plant extract is limited due to a lack of active ingredient characterization. Such bi-directional knowledge transfer should promote silicon farming.

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