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Function of Chelators in Nutrient Supply to Plants

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ABSTRACT: Plants require several elements to grow, some of which are readily available through the air, such as oxygen, carbon, and hydrogen. However, other essential elements such as magnesium, calcium, iron, and zinc are not created through photosynthesis and must be extracted from the soil. Fertilizers and plant nutrition play an important role in improving crop yield and quality. However, the use of chemical fertilizers has raised significant concerns about their impact on plant, animal, human, and ecosystem health. Chelates were first introduced to human nutrition and then to animal nutrition to improve nutrient status and combat deficiencies, particularly iron (Fe) and zinc (Zn) shortages. Chelates are organic compounds that help plants access nutrients that might otherwise be inaccessible due to soil conditions. The chelator molecule encases the ion (magnesium, calcium, iron, zinc, and others) and prevents it from reacting with other ions in the soil. Chelating agents protect metal ions from unwanted chemical reactions and improve their availability for plant roots. Different chelating agents exist, both synthetic and natural. Synthetic chelating agents include ethylenediaminetetraacetic acid (EDTA) and ethylenediamine di-hydroxyphenyl acetic acid (EDDHA). Natural chelating agents include amino acids, organic acids, and phenolics. Each type of chelating agent has a distinct role in improving nutrient bioavailability for plant uptake. It is preferable to utilize an organic and inorganic chelator mix to improve plant performance and yield.

Keywords: Photosynthesis, Fertilizer, Plant nutrition, Organic compounds.

INTRODUCTION

Plants get many of the elements they need through the air, oxygen, carbon and hydrogen are readily available. In addition, plants can create glucose and other substances through sunlight. However, basic element cannot be created through photosynthesis, and plants get extracted through the soil. The application of fertilizers and plant nutrition to the soil and plant has an inevitable role in yield and quality production of many agronomic as well as horticultural crops. Chemical fertilizers have been used extensively for decades to improve plant food productivity in agriculture, that in part has raised significant risk on plant, animal, human and ecosystem health qualities. Therefore, fertilizers and fertilization practices had an inevitable role in emerging new challenges. Chelates were first introduced to human nutrition and then to animal nutrition to improve nutrient status and to combat deficiencies particularly iron (Fe) and zinc (Zn) shortages. Chelators are compounds that bond to micronutrients, making them more readily available for uptake in plant cells. They are essential for plant growth and development (Sekhon, 2003).

What are Chelates?

In order to understand chelates, need to understand some things about the metal micronutrients such as iron, copper, zinc, magnesium and manganese. You may recognize some of these as being hard metallic substances, which they are. In order for plants to use them, the metal needs to be converted into a water-soluble form called ions. These ions float around in the water that surrounds soil particles. If they react with oxygen, they are converted into a form that plants can't use. They can also interact with other ions which may cause them to precipitate as solids, making them unavailable to plants. These ions float around in the water that surrounds soil particles. If they react with oxygen, they are converted into a form that plants can't use. They can also interact with other ions which may cause them to precipitate as solids, making them unavailable to plants. Chelates make it easier for plants to find certain nutrients. In fact, plants use chelates internally to move metal ions from roots to leaves. Chelates are clearly important for plant growth. Any chemical that has the properties described above has so-called chelating properties. Even glyphosate, the active ingredient in Roundup, acts like a chelate in soil.

Chelating agents

Chelating agents are the natural or manmade formed chemical compounds that react with metal ions forming a water-soluble stable complex. They are composed of a ring-like centre forming at least two bonds with the metal ion (Toso, 2014).

Chelation is a process that increases the availability of nutrients to plants. Chelated minerals are absorbed more rapidly by both plant roots and leaves, resulting in accelerated growth, higher Brix levels, and higher yield (Zuluag *et al.,* 2023). The chelation process is facilitated by chelating agents such as Ethylenediamine tetraacetate (EDTA), Diethylenetriamine pentaacetate (DTPA), Ethylenediamine dihydroxy-phenylacetic acid (EDDHA), fulvic acid, humic acid, and amino acids (Zhang and Zhou 2019). Chelates bind essential metal ions, increasing their solubility and uptake in plants (Haydon and Cobbett, 2007). They also prevent chemical reactions that turn some nutrients into insoluble compounds that are unavailable to plants (Bhatla *et al.,* 2007). Micronutrients such as iron, zinc, and magnesium are needed in relatively low quantities but are every bit as vital to a crops diet and healthy growth as macronutrients like potassium, phosphorus, and nitrogen. However, most of these necessary micronutrients are unavailable to plants while in their basic form because metals like iron and zinc have a positive charge, while the pores on plants wherein the metals would enter have a negative charge. The positively charged micronutrients cannot enter through the negatively charged pores. This is where chelates come into play. When a chelate bonds to a micronutrient, it surrounds or encapsulates individual ions and gives them a negative or neutral charge, allowing the nutrient to enter through the negatively charged pore and travel into the plant's tissues. Chelators are compounds that bond to micronutrients, making them more readily available for uptake in plant cells. There are several types of chelating agents used in agriculture, including synthetic and naturally occurring ones (Bhatla *et al.,* 2007).

Types of chelators used in agriculture

Synthetic chelating agents include:

1. Ethylenediaminetetraacetate (EDTA): It is a widely used chelating agent that binds to micronutrients such as iron, manganese, and zinc. It is effective in a wide range of pH levels but is not biodegradable.

2. Diethylenetriaminepentaacetate (DTPA): It is another synthetic chelating agent that binds to micronutrients such as iron, copper, and zinc. It is effective in acidic soils but has a limited range of pH tolerance.

3. Ethylenediaminedihydroxy-phenylacetic acid (EDDHA): It is a synthetic chelating agent that binds to iron. It is effective in alkaline soils but is expensive.

Naturally occurring chelating agents include:

1. Fulvic acid: It is a naturally occurring chelating agent that binds to micronutrients such as iron, copper, and zinc. It is effective in a wide range of pH levels and has the added benefit of improving soil structure and water retention.

2. Humic acid: It is another naturally occurring chelating agent that binds to micronutrients such as iron, copper, and zinc. It is effective in alkaline soils and has the added benefit of improving soil structure and water retention.

3. Amino acids: They are naturally occurring chelating agents that bind to micronutrients such as iron, copper, and zinc. They are effective in a wide range of pH levels and have the added benefit of improving plant growth and development.

Difference between organic and Synthetic Chelating Agents

1. Organic agents show more penetration rate than synthetic chelates, due to larger molecules such as EDTA, DTPA, EDDHA penetrate at slower rate.

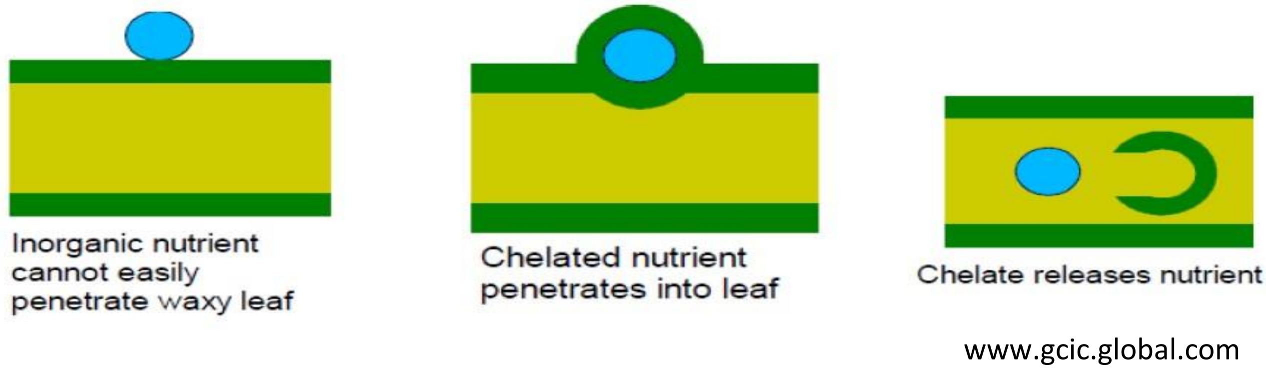
2. Organic chelates are biodegradable and non - toxic to the environment- E.g: EDTA forms chemically and microbiologically stable complexes that poses a threat of underwater contamination.

3. Organic chelates can be used as a food source to the micro - organisms while the synthetic cannot.

4. Organic chelating agents are more stable in comparison to synthetic chelating agents.

Chelation – Mechanism

The mechanism of action of chelators involves the formation of stable complexes between the chelator molecule and the metal ion. The chelator molecule forms multiple bonds with the metal ion, creating a ring-like structure called a chelate. This ring-like structure prevents the metal ion from reacting with other molecules or forming insoluble compounds that are unavailable to plants. Leaves have a waxy coating which prevents them from drying and repels water and inorganic substances which making it difficult for inorganic nutrients to penetrate into the Leaf.



1. The organic coating around the chelated nutrient allows it to penetrate through the wax into the leaf.
2. In the leaf, the chelate releases the nutrient so that it can be used by the plant.

Significance of chelation process in soil

1. Increase in available nutrients: In the alkaline soils, chelating agents bind to the insoluble iron and make them available to plants.

2. Prevents nutrients from forming insoluble, unavailable compounds: Chelating agents increase the availability of metal ions for plant uptake by protecting the chelated ions from unwanted chemical reactions.

3. Chelates reduce toxicity of some metal ions: Substrate chelation reduces the concentration of metal ions to a normal beneficial level. This is done by the humic acid and several high molecular weight compounds which are present in organic matter.

4. Chelates prevent nutrients from wash out: Chelate forming metal ions are much more stable than free ions.

5. The chelation process increases the mobility and therefore availability of nutrients to plants. By this increased mobility the uptake of nutrients by plants is enhanced.

Chelating agents reduces the growth of plant pathogens by reducing available iron: Chelating agents may sometimes suppress the growth of plant pathogens by depriving iron hence favoring plant growth.

Benefits of using chelated nutrients

Chelated nutrients are essential for plant growth and development. They are micronutrients that are bonded to chelating agents, which make them more readily available for uptake in plant cells. There are several benefits of using chelated nutrients in agriculture.

1. Improved nutrient uptake: Chelated nutrients are absorbed more rapidly by both plant roots and leaves, resulting in accelerated growth, higher Brix levels, and higher yield. Chelation increases the solubility of metal ions, making them more available for uptake by plant roots. Chelated minerals are absorbed more rapidly by both plant roots and leaves, resulting in accelerated growth, higher Brix levels, and higher yield.

2. Prevention of nutrient deficiencies: Chelated nutrients prevent nutrient deficiencies in plants. Micronutrients such as iron, zinc, and magnesium are needed in relatively low quantities but are every bit as vital to a crop's diet and healthy growth as macronutrients like potassium, phosphorus, and nitrogen. However, most of these necessary micronutrients are unavailable to plants while in their basic form because metals like iron and zinc have a positive charge, while the pores on plants wherein the metals would enter have a negative charge. The positively charged micronutrients cannot enter through the negatively charged pores. This is where chelates come into play. When a chelate bonds to a micronutrient, it surrounds or encapsulates individual ions and gives them a negative or neutral charge, allowing the nutrient to enter through the negatively charged pore and travel into the plant's tissues.

3. Improved soil structure: Chelated nutrients improve soil structure by increasing water retention capacity and reducing soil erosion. Fulvic acid and humic acid are naturally occurring chelating agents that improve soil structure and water retention.

4. Increased crop quality: Chelated nutrients improve crop quality by increasing the nutrient content of crops.They also improve the flavor, color, texture, and shelf life of fruits and vegetables.

5. Cost-effective: Chelated nutrients are cost-effective because they reduce the amount of fertilizer required for crop production. They also reduce the amount of fertilizer runoff into waterways, which can cause environmental damage.

Chelating agents for increasing nutrient availability in soil

Chelators or ligands when combined with a nutrient, can form a chelated fertilizer (Lopez-Rayo *et al*., 2015). Chelated fertilizers are protected from oxidation, precipitation, and immobilizationin certain conditions because the organic molecule (ligand) can combine and forma ring encircling the nutrient. The pincer-like manner in which nutrient is bonded tothe ligand changes the nutrient's surface property and favors the uptake efficiency of foliarly applied nutrients (Tewari, 2018).

Need of Chelated fertilizers

Soil is a complex and heterogeneous environment where nutrient availability can be reduced or increased due to various factors. Some nutrients can get oxidized or precipitated, making them unavailable to plants. Chelation is a process that prevents these nutrients from undergoing such chemical reactions. Chelated fertilizers increase the availability of micronutrients such as Fe, Cu, Mn, and Zn, which in turn increases productivity and profitability. Chelated fertilizers perform better in soils with pH greater than 6.5 (Liu *et al.*, 2012). To ensure a good crop yield, Crop Nutrient Requirements (CNRs), including micronutrients, must first be satisfied from the soil. If the soil cannot meet the CNR, chelated sources need to be used. Iron is mainly utilized as Fe^{2+} ion in plants. This can be readily oxidized to the unavailable ferric form (Fe^{3+}) in the plant when pH of the soil is greater than 5.3. Iron deficiency is often observed in soil having pH greater than 7.4. Application of chelated form of iron can prevent the conversion from Fe^{2+} to Fe^{3+}. Nutrients such as Fe, Mn, Zn, and Cu are present as positively charged metal ions in soil solution and will freely react with oxygen and hydroxide ions, making their application to soil inefficient (Tewari, 2018).

Chelates in Zn Nutrition. Zinc fertilizer derived from organic sources comprises chelates of EDTA, NTA, and HEDTA, in addition to Zn-ligninsulfonate, Zn-polyflavonoid, and wood pulp industry byproducts (Hussein *et al*., 2019). Although zinc sulfate is a typical inorganic form of zinc, specific soil conditions can limit its solubility and plant availability (Montalvo *et al.*, 2016) Approximately 85-90% of zinc supplied to the soil is fixed in various ways, making it unavailable to the plant (Sekhon, 2003). With a zinc content of roughly 12-13%, Zn-EDTA (Na_2 Zn-EDTA) is the most widely used source of zinc in chelated form (El-Nagy *et* *al*., 2020). In high pH soils, chelated zinc dissociates relatively little and, because it is negatively charged, travels readily like other anions to the area around the roots. In general, reports have indicated that organic-chelated zinc sources are preferable to inorganic zinc sources (Sekhon, 2003).

Mn and other Chelates. In soil, chelated-Mn reactions differ significantly from chelated-Zn reactions. The significant amount of accessible iron in our soils makes Mn-chelates useless when applied to the soil. Mn in soil-applied Mn chelates is replaced by Fe. Thus, Mn-chelates are effective only when used as liquid fertilizer formulation and hydroponics. In calcareous organic soil, foliar Mn treatment is often advised (Lopez-Rayo *et al*., 2015). Fungicides that include manganese, like Maneb, have also shown promise in treating crop deficiencies in fruit trees and other plants (Ali *et al*., 2016). The application of Cu chelates containing various amino acids resulted in an increase in grain production, amino acid content, absorption, and chlorophyll content (Lopez-Rayo *et al*., 2015; Hussein *et al*., 2019; Souri, 2016). Additionally, it affected the amounts of Cu, Zn, and Mn in grain, straw, and roots (Kumar *et al.,* 2009; Zhang *et al.,* 2020). When tested with mixed and Zn-chelated micronutrients, watersoluble chelates of hydrophilized and degraded Larch tanin with Fe, Mn, Zn, and Cu ions improved leaf yield by 20-25% in apples and 26.5% in Ginkgo biloba (Sekhon, 2003).

Amino Acid Chelators. True amino acid chelates are emerging as state-of-the-art technology for delivering selected micro nutrients with maximum bioavailability, tolerability and safety (Hussein *et al*., 2019; Byrne and Murphy, 2022). These are chelated mineral products specifically designed for application on plants. They are unique because the micronutrients are chelated with amino acids. The advantages of using these chelated micronutrients are that the amino acid ligands surround and protect the micronutrients from adverse interactions - typically those that take place in soil solution, in the presence of soil or on leaf surfaces (Jacob *et al.,* 2022). Natural amino acids are used to chelate the micronutrients and hence they are rapidly absorbed, translocated and metabolized by plants (Nawrocki, 2020; Singh, 2020). Furthermore, because they are tiny molecules, they are absorbed and moved around in the plant in a manner comparable to that of other tiny molecules that contain nitrogen. They can all be absorbed by plants because they are all fully soluble in water (Sekhon, 2003). The leaves of most plant as well as primary cell wall serve as a barrier against the absorption of free metal ions. Metals completely chelated with amino acids are neutral in charge. They are neither attracted to nor repulsed from negatively charged surfaces of the leaf. Therefore, they freely pass through this barrier. When the amino acid chelates reach the cell membrane, they are recognised by the mechanisms of absorption as a source oforganic N. As a result, entire amino acid chelate is taken into the cell very rapidly and efficiently.

CONCLUSION

Chelators play an important role in plant nutrition by increasing the availability of micronutrients to plants. They help accelerate growth, increase yield, and improve crop quality. Chelation is a process that enables micronutrient uptake in plant cells by bonding to micronutrients. Chelating agents such as EDTA, DTPA, EDDHA, fulvic acid, humic acid, and amino acids facilitate this process. There are several types of chelators used in agriculture, including synthetic and naturally occurring ones. Each type of chelator has its own advantages and disadvantages depending on the soil type and crop requirements. The possible benefits of using chelators and minerals as an organic plant fertilizer include reduced plant nutrition costs, improved performance, and a high potential for antioxidant and antibacterial effects. Based on the results, it was proposed that, in order to get the best results in plant nutrition, the minerals might be supplemented in a combination of inorganic and organic sources at the two-third and one-third levels of requirements, respectively.

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