

Review

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Aminochelate fertilizers: the new approach to the old problem; a review

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Abstract: Aminochelate fertilizers are the latest novelties regarding plant nutrition in agricultural production systems. They are part of the modern formulae of fertilizers which are synthesized based on various amino acids, mainly glycine. In recent years, they have had a rapid growth in the marketplace. Their rapid growth in formulations, manufacturing, diversity and application is mainly due to the novel understandings regarding diverse roles of amino acids in plant metabolism. Compared to routine fertilizers or other commercially synthetic chelators such as EDTA; however, aminochelates represent a safer and more efficient form of fertilizer, resulting in better plant performance and less environmental risks. Aminochelates represent effective fertilizers for both soil and particularly for foliar applications. Despite, aminochelates having quickly dominated the fertilizer markets in many countries, there is not enough scientific data and information regarding detailed responses of crops to these types of fertilizers. This in part, may be due to their mixed composition of several nutrient elements, giving various nutrients effects, meaning that conducting scientific experiments and concluding remarks, , would be very difficult. This review provides information concerning different aspect of aminochelate fertilizers including their history, structure, types, value and effects on agricultural crops.

Keywords: Aminochelate; Fertilizer; Environment; Amino acid; Chelate; Plant Nutrition

1 Introduction to the background

Climate change and unsustainable approaches and practices have imposed many threats on agricultural food production [43]. Various practices towards organically instead of chemically procedures, play an important role in agricultural production management; so, new adaptive strategies are always necessary to cope with all new emerging challenges. During last the decades, application of various chemical fertilizers has raised significant risk to plant, human, animal and ecosystem health qualities [6, 23, 39, 40]. For decades, soil fertility and quality were adversely affected by many fertilizing strategies in world-wide agriculture section. Routine chemical fertilizers, aimed at increasing yield and quality, frequently resulted in reduced soil quality [23, 37], and various environmental pollutions [41]. However, the best management practice regarding quality of foods and environment, is organic production, as well as no, or reduced, application of fertilizers and pesticides in conventional farming systems.

General chemical fertilizers are in simple forms which normally have low efficiency rates. Therefore, they are used in high amounts for a given yield and quality. So, during the last few decades, due to their high application rates, low efficiency and application methods, they had a dominant role in various environmental challenges [37].

Micronutrient metals such as iron, zinc, manganese and copper are essential nutrient elements required for healthy plant growth, as well as for structural and catalytic roles in proteins which are involved in metabolism and development [16]. Lime-induced chlorosis is one of the most important plant nutritional disorders, mainly due to micronutrients deficiency, in particular Fe deficiency, affecting many yield and quality parameters. In general routine chemical salts, with high reactivity and low efficiency, are not effective in correction of micronutrient deficiencies especially in the case of iron deficiency [20, 35, 12]. During the last few decades various chelating agents were introduced and applied in cropping systems particularly in horticultural sections to combat different deficiencies, in which routine fertilizers were not able to correct them. Therefore, different synthetic chelates were

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used extensively in soil and in hydroponic systems to keep, or even to improve, the micronutrients bioavailability and plant tissue concentrations [20, 35]. Therefore, in many cases, only the use of chelated forms of micronutrients could meet the plant's requirements for nutrients to provide healthy growth and high yield achievements [13, 37]. Nevertheless, chelation is a natural plant response to nutrient limitations, particularly under iron and phosphorus deficiency [23, 35, 21, 40].

Aminochelate fertilizers are the latest novelties regarding plant nutrition in agriculture [37]. They are among the new and modern formulae of fertilizers which are synthesized based on various amino acids. Application of aminochelates instead of simple routine fertilizers generally results in higher nutrient uptake efficiency [39, 12, 10] and less negative side effects [37].

Application of aminochelate fertilizers by farmers has increased during recent years [39]. In countries such as Iran they are the dominant form of fertilizers on the marketplace [37] and many farmers are familiar with various aminochelate fertilizers, claiming their higher effectiveness on plant growth and on correcting nutrient deficiencies. However, on a worldwide scale, many products which claim to be amino acid chelates, may be just a mixture or complex, but not real chelates. Due to their reputation among farmers and premium higher price of these types of fertilizers, it seems that more than 50% of those present in the market are not real chelates [37]. Nevertheless, nowadays various types and brands of aminochelate fertilizers exist for single or several nutrients, which are mainly produced by several American and European companies.

2 Definition and structure of aminochelates

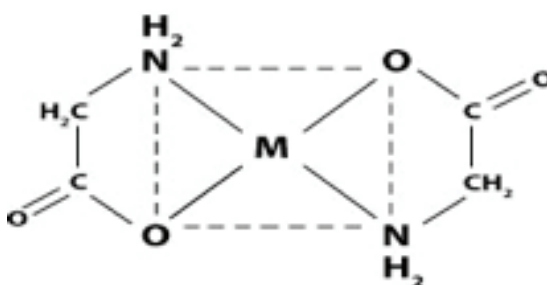
Chelators or chelating agents are chemical compounds which have a higher affinity to bond tightly with a metal ion [37, 35, 5, 20], forcing the metal atoms to follow the chelating molecule. The chelating effect is mainly due to several bonds by which a ligand molecule can enslave a single metal ion [37]. In other words, a chelating agent is a multidentate ligand, forming at least two- and up to eight bonds to a single metal ion, protecting it from unwanted reactions in the soil and inside the plant [37].

All chelating agents have an organic structure, but they are different as naturally occurring molecules such as organic acids and amino acids, or as synthetically commercial products such as ethylenediamine-tetraacetic

acid (EDTA). Aminochelates are amino acid-based chelate fertilizers of single or several micronutrients [37], although aminochelate-containing macronutrients also exist widely in the marketplace. Aminochelate fertilizers are synthesized using reactions of amino acids (two-three moles) with metal nutrients from a soluble metal salt (one mole), resulting in coordinate covalent bonds [35, 5, 37]. Aminochelates as bi-dentate ligands, form relatively strong chemical bonds with positively charged metal atoms [37, 3]. However, certain combinations of minerals and amino acids, because of weak chemical bonds, may not produce good chelate molecules.

After production, aminochelates must have some quality control factors including [37]: **proper molecular weight**; despite all amino acids having the potential to be used for aminochelate production, those with molecular weight up to 150-200 g are most suitable. The resulting aminochelate molecular weight must not exceed 800 Dalton. Small amino acids such as glycine are preferred in this regard. They need to be small enough to be taken up easily by leaves or plant roots. **Proper electrical charge**; it is also necessary that the aminochelate produced must be electrically neutral, but with enough stability constant to avoid various chemical interactions prior to absorption. Aminochelates also need to have **high water solubility** and **plant availability**, to be simply metabolized inside the plant. The composition and content of elements of aminochelate fertilizers must be declared on any product.

In aminochelate fertilizer manufacturing plants, glycine technology is involved in any patented processes. Glycine, as the smallest amino acid, is very suitable for production of various metal ion chelates, creating fully chelated products [37, 35, 5]. In Fig. 1 the schematic chemical structure of a potent metal chelate is presented.



The structure of a real metal chelate enclaved by two molecules of glycine

Figure 1: The structure of a real metal chelate, in which each molecule of metal is captured by two molecules of glycine forming two ionic and two coordinative bonds.

3 History of aminochelates

In current agriculture, application of chelate fertilizers plays an important role in the production process of many crops in particular horticultural and greenhouse plants. Despite chelating reactions being discovered about 100 years ago, their application and importance in agriculture was not fully realized until 50 years later [29, 37]. The term “chelate” was first used by “Morgan and Drew” to describe compounds which produce complexes with metals, to be used as additives in human or animal nutrition [29]. In beginning of the 1950s, iron chelates were used for the first time to correct Fe deficiency in plants [19]. Later in the 1960s scientists tried to produce and feed animals with metal aminochelates, so, various amino acids, as effective ligands for bonding to metal ions were considered as the best candidates [29, 7]. From then, many studies were conducted on aminochelates, mainly in human and animal nutrition. However, application of aminochelates in plant nutrition was not attractive until recent years [37]. Nevertheless, human and animal sciences compared to plant science are more advanced regarding aminochelate applications, as well as with regards to various scientific information and investigations which are available in data banks. Nowadays, despite the lack of adequate data on aminochelates, in many parts of the world they are the dominant forms of fertilizers in the market.

4 Various types of aminochelates

Chelates and aminochelates were first released as Fe chelate to improve iron concentrations in biological systems, basely as additives in human and animal nutrition [17, 2, 7, 29]. Later, they were also extended to other metal nutrients, and nowadays aminochelates of almost all cationic and anionic forms of nutrient elements exist in the marketplace. For example, ferrous bis-glycinate was the first aminochelate synthesized and used as a food additive in human and then in animal nutrition [29, 5, 1]. It is only less than two decades ago that this compound has been utilized as an aminochelate fertilizer in plant nutrition. In other words, there has been a 2-3 decades lag period between application of aminochelates in plant science and their commercial application in human and animal nutrition.

Nowadays in agriculture, aminochelates supply a wide range of nutrient elements to various crops by soil or foliar applications. In the market, there is a wide diversity of aminochelate fertilizers both in terms of amino

acids and nutrient elements [37, 39]. Nevertheless, glycine is the major amino acid in aminochelate-based plant nutrition. The wide diversity of aminochelate fertilizers in the market is mainly due to their high acceptance by farmers in many parts of the world. On the other hand, different aminochelate fertilizers are produced as powder or in liquid form, using a single metal ion or in combination of several nutrient elements [9], giving the farmers a wide range of options. Some aminochelate formulations contain all nutrients required for normal plant growth and development, and therefore could be regarded as a nutrient solution formula [37]. Nevertheless, many fertilizer products in the marketplace, despite claiming to be aminochelate, but they are just a “complex” or “organic salt”.

In many countries aminochelates have quickly dominated the fertilizer markets; however, there is not enough scientific data and information regarding detailed responses of crops to various aminochelate fertilizers. This in part, may be due to the mix composition of several nutrients, making conducting scientific experiments and concluding remarks, because of the various nutrients effects, quite difficult. Therefore, manufacturing companies are required to produce various single nutrient aminochelates, by which detailed information on plant responses could be achieved.

5 Effects of aminochelates on plant growth

In the science literature, it is quite difficult to find a detailed and deep informative study on aminochelate's effects on plant metabolism. However, several well designed recent experiments highlighted the value of aminochelate compounds as effective and suitable fertilizers for agricultural applications [8, 12-14, 22, 26, 27, 30, 38, 39].

Foliar spray of certain Zn-amino acid chelates including Zn-arginine, Zn-glycine and Zn-histidine on the yield and grain quality of wheat cultivars under field conditions showed that grain Zn, Fe and protein concentrations were on average 14.3% higher in wheat plants sprayed with zinc aminochelates than those sprayed with ZnSO_4 [13]. In addition, foliar application of Zn fertilizers resulted in significant decreases (on average 17.9%) of grain phytic acid [13]. In another study by synthesis of three zinc aminochelates i.e., Zn-arginine, Zn-glycine and Zn-glutamine and their application on yield and nutrient elements, uptake by lettuce grown in nutrient solution under salt stress, it was shown that zinc aminochelates could partly alleviate the

damages (induced by salinity) on root and shoot growth of lettuce. However, glycine was more effective in this regard compared to the other two amino acids. Under salt stress, the highest increase in Fe and Ca concentrations was achieved by zinc-glycine aminochelate, while the other two amino acids resulted in the highest K concentration in roots and shoots of lettuce [25]. Similarly, by synthesis of Iron(II)-amino acid chelates of Fe-glycine, Fe-arginine and Fe-histidine and their evaluation on salt-induced damages in tomato plants compared to Fe(II)-EDTA, it was shown that the adverse effect of salt stress was significantly ameliorated by using Fe(II)-amino acid chelates. Shoot Fe, Zn, N and K contents were decreased by salinity while increased using Fe(II)-amino acid chelates. Application of Fe(II)-amino acid chelates increased activity of catalase (CAT) and ascorbate peroxidase (APX) in the leaves of tomato plants exposed to salt stress [14].

In marigold (*Calendula officinalis*) by foliar application of some aminochelate fertilizers, it was shown that four foliar applications of various aminochelates in a concentration of 0.25% have resulted in significant improvement in plant growth parameters such as plant height, number of flowers, length of flower stem, plant fresh and dry weight and leaf N concentration, compared to soil applied NPK [39]. In chilli plants (*Capsicum annum* L.), foliar application of organically chelated micronutrients of iron, zinc, copper and manganese (with three doses of 0.5, 1.5 and 2.0 %) showed that the maximum plant height, number of branches, leaf area, fruits and total yield per plant were obtained in 1.5 and 2% concentrations [8]. Foliar application of three different amino acid chelates, namely Fe-, Zn- and multimineral- amino acid chelates, has resulted in significant higher leaf Fe (112%), Zn, Mn, and Cu concentrations and 64% higher yield in seedlings of Williams pear [18]. Foliar application of calcium-micronutrient aminochelate fertilizers on Kabkab date trees significantly increased fruit weight, fruit length and fruit TSS [27]. In another study by hydrolysis of chicken feathers, natural Fe and Zn amino acid chelates were synthesized and by their application on rice they showed nearly 10 % more efficiency compared to their EDTA fertilizer [26]. Application of 1% calcium aminochelates from three sources of lysine, threonine or methionine compared to calcium chloride in nutrient solution on *Lisianthus* showed that aminochelate fertilizers significantly improved calcium concentration in flowering stems, number of flowers and the postharvest life of *Lisianthus* cut flowers [33].

In soybean, treatments of amino acids significantly improved growth parameters of shoot fresh weight and pod yield [32]. The effects of amino acid mixtures of

alanine, serine, phenylalanine and tyrosine fertilization through the nutrient solution on growth variables and leaf mineral concentration of tomato plants showed that leaf Ca, K, Fe, Cu, and Mn concentrations were improved, and resulted in higher a chlorophyll concentration, plant height, and lateral shoots in tomato plants [10].

Foliar application of a mixture of amino acids as “Amino Total” containing 17 amino acids, in different concentrations of 500, 1000 and 1500 mgL⁻¹ on bean plants showed that the highest level of amino acid of 1500 mg L⁻¹ exerted the strongest effect in alleviating the harmful effect of salinity stress on bean plants [31].

Positive and constructive effects of aminochelates are predicted for many plant growth parameters, since there are some naturally occurring chelators including amino acids, peptides, proteins, organic acids, lignin and phenolics, which are nutritionally interesting with particular importance [37]. In addition, organic substances from organic fertilizer sources, or produced by plants or microorganisms, are natural chelating agents which play important roles in nutritional competence among plants [21, 40, 41].

Various investigations show that foliar or soil application of aminochelates could lead to improved nutrient uptakes compared to soil application of routine chemical fertilizers [14, 15, 10]. Improved plant growth and performance, as well as higher yield and quality are obtained by application of aminochelate fertilizers compared to routine chemical fertilizers such as sulfate salts [13]. There is also a superior effect of aminochelates application even compared to other synthetic chelates such as EDTA and EDDHA on many plant yield and quality traits [34, 26, 12].

On the other hand, aminochelates with considerable amounts of nitrogen in form of amino acids, play an important role in supply of plant's nitrogen requirements. They may contain nearly about 2-20% N-amino acid [37]. Nitrogen is often considered as the most important nutrient element in plant growth and productivity. Nitrogen is the main, and iron is the second, limiting factor for optimum plant growth and yield production in many agricultural systems. Aminochelates normally contain both of these nutrient elements, as well as several other micronutrients (and sometimes macronutrients). Amino acids in form of aminochelate could help to improve nutrient uptake and their internal translocation efficiency [4, 37].

Amino acids represent a more suitable form of nitrogen for plant uptake and assimilation [23, 11]. The absorption of amino acids could also play an important role in improving efficiency of nitrogen as well as many micronutrients particularly iron [23, 24]. High concentration of N in aminochelate fertilizers could explain their superior

effects on plant growth and productivity. This is particularly highlighted when N present as amino acids which normally have higher uptake efficiency by roots or even by foliar application [9, 35]. It has been shown that plants can uptake various nitrogenous compounds including amino acids by root as well as by leaves [2, 21, 23, 28]. In addition, at the molecular level, amino acids have their own transporter proteins, although they can be taken up by membrane channels as well [42, 44].

Under limitation of nutrient elements availability, foliar application of their aminochelate fertilizers could rapidly and effectively result in plant leaf recovery [37, 36, 15]. Application of amino acids in nutrient solution could also improve mineral composition of plant leaves resulting in higher chlorophyll concentrations and delay of leaf senescence [10]. From another perspective, amino acids are also considered as precursors for protein synthesis, indicating their importance for stimulation of cell growth. Because of their carboxylic and amine groups, they represent an important plant cell buffering compound, and help to maintain a favorable pH value for optimum cell functioning. Amino acids can directly or indirectly influence the physiological activities in plant growth and development, as exogenous applications of aminochelates have been reported to modulate the growth, production and quality of tomato seedling [38]. Uptake studies regarding aminochelates, however need to be evaluated by labeling the iron amino acid chelate with radioactive or stable iron isotopes and then measuring the amount incorporated into different metabolic pools during a course time.

6 Conclusion

The effect of aminochelates in plant growth is not yet sufficient clarified. Aminochelate formulation is a new progress in plant nutrition. Various studies mentioned in this review revealed that they have a superior effect on plant growth and productivity compared to simple chemical salt fertilizers. Aminochelates represent a more efficient and safer form of fertilizers in plant nutrition, without environmental side effects. The aminochelates are certainly suitable for specific conditions, such as iron deficiency correction in calcareous soils. Progress in aminochelates formulations and application may in future lead to them becoming the dominant strategy in plant nutrition. Application of routine fertilizers as well as commercial synthetic chelators like EDTA is not regarded as a sustainable practice, and in this regard aminochelates

represent a suitable candidate to replace those fertilizers. Although aminochelates first evolved as food additives in human nutrition to combat iron and zinc deficiencies, nowadays they have a wide diversity as effective fertilizers for agricultural application. In their future, it is important to know whether nutrient absorption (such as iron) from these fertilizers is different for various elements or amino acids, and even for soil versus foliar application.

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