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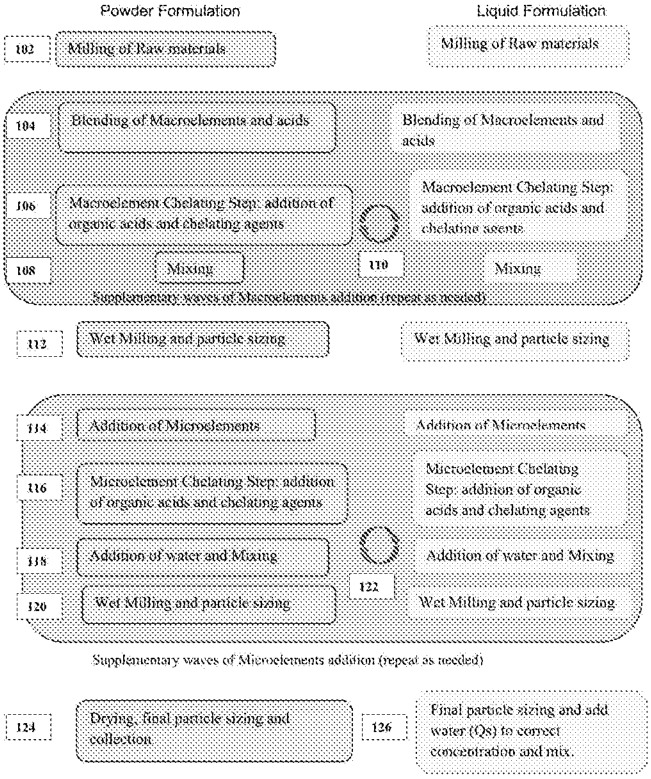
(54) **Nano-chelated complexes.**

(57) The invention relates to nano-particles of chelated complex compounds useful as chelate fertilizers, each said compound comprising: a chelate complex core made of at least one polycarboxylic acid incorporating therein at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof, said chelate complex core further comprising at least a second cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC), or mixtures thereof, forming nano-chelated complex compounds, wherein the particle size thereof is 100 nm. Up to 17 first and second cationic compounds are present on the nano-particles of chelated complex compounds. The invention also concerns a process for preparing said nano-chelated complex compounds.



Nano-chelated complexes

The invention relates to the field of nano-chelated complexes useful as chelate fertilizer in various agriculture fields.

In respect to importance of soil fertilization as a global food security key or sustainable agriculture and also the role of micronutrients and macro element usage; a maximum productivity in terms of quantity and quality of agricultural products needs to be achieved on the one hand and on the other, barriers such as deficiencies of available elements in soils, their calcareous conditions, high pH and water salinity and lack of elements balance in soil and excessive chemical fertilizer usage that cause soil degradation and elements disturbance.

Existing fertilizer, with high consumption and low deficiency, do not have an efficient effect on elements absorption, to nutrients balance and remove nutritional needs. Modern agriculture requires that many products be used (in combination) in order to cover these deficiencies, often leading to high costs

Excessive usage of chemical fertilizer has disturbed soil and subsoil waters, creating various diseases and carcinogens in growing societies reflects the need of designing products that have no negative effects

Elevated use of urea and phosphate fertilizers in agricultural practices converts to nitrate and cadmium, where it accumulates within the produces. Nitrates and other converted heavy metals are considered as carcinogenic substances that causes gastrointestinal cancer, neurological abnormalities and disorder in endocrine system and immune system. In addition to carcinogenicity, it causes stunting and disorder in renal function.

Based on Liebig's law of the minimum, nutrients usage should be fit to plant’s need and all elements should be available according to the requirements of the plant’s growth stage. The balance between elements is very important and needs to be reflected with a proper balance of different concentration of elements in the soil and plant absorption pathways (root base structure and leaf surface).

In recent years, a high consumption fertilizer usage has been in combination with ethylenediaminetetraacetic acid (hereinafter "EDTA") chelating agents. This new technology provides the ability to apply fertilizers in a more efficient manner and in different types of application (i.e. foliar sprays). Most of the available chelated fertilizers are mono element or a combination of elements that are used as fertilizers, with relatively low percentage in terms of concentrations. According to research performed, in both land and hydroponic environments, while the concentration of minerals chelated with EDTA increased, it was noticed that plant uptake did not follow due to the high molecular weight of the EDTA ligand. The molecular weight and negative charges profile of EDTA-chelated minerals, the adsorption of the elements requires increased energy and reduces the performance within the plant absorption in transporting the chelated minerals through the cellular walls, which reduces their root structure and shoot length.

Chelate compounds, i.e., chelating agents, chelate complexes, chelants, chelators, and/or sequestering agents, have numerous commercial applications, such as, for example, plant nutrition as fertilizers, and animal nutrition and treatment as supplements and medicines, respectively. Known chelating agents include EDTA and ethylenediamine-N,N'-bis(2-hydroxyphenylacetic acid) (hereinafter "EDDHA"), and known chelate complexes include iron-EDTA (hereinafter "Fe-EDTA") and iron-EDDHA (hereinafter "Fe-EDDHA").

Fertilizers that contain Iron (Fe) elements are also of interest and made by different bases such EDDHHA – HEDTA – EDDHA –OTPA –EDTA in recent years. EDDHA also does not deliver high percentage of Iron or other elements, such as Felixper 6% EDDHA (Germany) and Omex Iron chelated (England) and Grow More 6546 EDDHA Iron Chelate and others. These fertilizers are expensive and technology base on (Ortho-Ortho) or (Ortho-Para) or (Para-Para) Isomers that are stable, semi stable and unstable, were used respectively.

In recent year, there has been a focus on Iron chelated fertilizers within the market. It should also highlight the need for equilibrium of multiple elements in plants to promote optimal and healthy plant growth.

The rhizosphere is a microecological area in the immediate vicinity of the plant root, where rapid and numerous chemical interactions occur. Its environment is more competitive than the soil mass. Compounds added to the soil by the roots are classified into four categories: exudates (passively removed from the roots), secretions (actively removed from the roots), dead cells, and gaseous compounds. The chemical and biological processes that take place in the rhizosphere not only determine the mobility and uptake of soil nutrients, but also control the efficiency of nutrient consumption. Establishing an integrated nutrient management strategy in the root zone is an effective way to solve the problem; along with high product yields, nutrient efficiency and environmental protection. It is estimated that decreasing each unit of acidity potentially increases the absorption 100 times.

The pH regulation is one of the most important factors for optimizing mineral availability for plants. Acidic soils are defined as having a pH under 4.5. At this pH level, elements such as iron, aluminium and manganese become significantly soluble and can lead to toxicity in plants. When soil pH reaches 5.5, nitrogen will be most available for plants. When soils reach levels between 6 and 7, phosphorous is at its optimal availability for plants.

There are no current chelate combination available for enhancing plant absorption and improved efficiency. Besides, there is always a need to improve chelated fertilizer in agriculture in terms a broad pH stability when used *in situ*, lowered potential for soil toxicity, increased absorption ability of a mineral by the plant, using a process of manufacture thereof without any need of heat, adjuvants, additives, i.e. silicon dioxide, titanium dioxide, catalysts, solvents, surfactants, dispersant and/or preservatives, among others.

For solving at least one of the above needs and/or drawbacks, the invention provides nano-particles of chelated complex compounds useful as chelate fertilizers each said compound comprising:

a chelate complex core made of a at least one polycarboxylic acid incorporating therein

- at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof,

said chelate complex core further comprising

- at least one second cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC), or mixtures thereof, forming nano-chelated complexes compounds,

wherein the particle size thereof is ≤ 100 nm.

Such nano-particles of chelated complex compounds, presenting a particle shape, exhibit reduced surface tension force and increase contact surface of leaves and/or root structure of a plant, accelerated cell membrane crossing and plant vascularization, increased absorption ability, decreased consumption during plant growth, lowered potential for soil toxicity due to non-fixation in soil and higher economic efficiencies. In other words, said compounds optimize plant absorption of various elements that are in soil and provide proper balance in order to promote optimal growth, yield, as well as eliminating deficiencies in plants.

Moreover such nano-chelated complexes present stable profile within a pH range of 3 -8.5. This stability profile is especially important as agriculture soils vary widely from region to region and country to country. Said compounds are stable but bio-available to plants.

One of the main aspects of the invention, is that the particles size of said nano-chelated complexes is not higher than 100 nm and that the chelate complex can support high concentration of elements. Such particle size of the nano-chelated compounds reduces surface tension and increase contact surface of plant surfaces, such as root, leaf, stem and fruit, with fertilizer particles, as well as increases the efficiency to penetrate cell walls and nutrient absorption.

In the context of the invention, “nano-particles of chelated complex compounds”, otherwise named ”nano-chelated complexes” or ”nanoparticle(s)” are generic complexes between the at least one polycarboxylic acid and the first cationic compound, otherwise named ”core macroelement”, and the second cationic compound, either named “microelements” or “macroelements” depending on the element added, are created, for example named “nano-chelated complexes”.

The nano-chelated complexes improve the delivery and collection of various elements and/or metal ions in all pH environments, including highly acidic and alkaline environments. The unique arrangement of the atoms and molecules due to self-assembly of the nano-chelated complexes results in the formation of a structure exhibiting higher resistance against structural breakage and/or deformation in highly acidic or alkaline environments.

The customizability options of the nano-particles to deliver or collect different elements and/or metal ions enables the nano-chelated complexes to be optimized for various uses. The nano-chelated complexes can have a tailor-made approach to farming if required, based on the soil characteristics and the desired crop.

The nano-chelated complexes produced are environmentally friendly and can be used for all types of agriculture; Crops (farms and greenhouses), Horticulture, Orchards, Plants, Flowers, Forestry.

While a single or multiple source element can be received within the polycarboxylic acid, combination up to 17 source elements, i.e. first and second cationic compounds, within the polycarboxylic acid in a stable fashion, could be done to obtain a stable structure of nano-chelated complexes. In some embodiments, the common use will dictate the necessity to be between 1 to 14 elements for agricultural purpose. Consequently, a mixture of various individual nano-particles is obtained. In said mixture, each individual nano-chelated complex may include at least one of the first cationic compound, such as N, and at least one second cationic compound, such as Zn. In some embodiments, and depending on conditions of the process for obtaining thereof, each individual nano-particle may include 1 or more, preferably of from 1 to 14, of the first cationic compound, which could be identical or different, and of from 1 to 14 of the second cationic compound, which could be identical or different, the number of both said cationic compounds being less than 17, more preferable of from 9 to 17, or 10 to 17, even better 11 to 17 or 12 to 17.

According to an advantageous embodiment, without being bound by any theory, a nano-chelated complex includes a chelate complex core structure of the polycarboxylic acid and the at least the first cationic compound, wherein the at least one first cationic compound is embedded or encapsulated within the polycarboxylic acid, and further the second cationic compound, wherein the particle size is less than 100 nm. Preferred chelate complex core structure is when N or P is the first cationic compound, leading to a robust chelate/complex structure that renders the final compound, nano-chelated complexes, stable and efficient in terms of uses in agriculture.

In the context of the invention, the “particle size” of the nano-chelated complexes has to be understood as the largest measured mean diameter of the whole/various particles forming the nano-chelated complexes, said particles, as a whole, presenting various shapes including, for example, spherical, ovaloid or rod like shapes. Without being bound by any theory and in some instances, the mean diameter of each particle is less than 100 nm. For example, if the particle is ovaloid, then the particle size thereof represents the diameter or a distance between two points at the end of each particle edge. Consequently, each particle has a particle size of less than 100 nm, regardless its shape, but it should be understood that the largest diameter or a distance between two points at the end of each particle edge, as defined above, is less than 100 nm.

When the produced nano-chelated complexes are used as fertilizers in agriculture, they have a positive effect on increasing the yield of crops, enhancing the crop nutrient profile, improve the crop robustness for transport and increasing the shelf-life, due to improved retained water profile, and eliminate the risk of fertilizer toxicity, due to the significantly lower quantity of fertilizer needed, for example between 7 to 20 less than traditional fertilizers. The use of the described fertilizer has the ability to increase the resistance of plants against pests, temperature fluctuations and other threats from the environment. In addition to benefits to the crops and agriculture, the use of the nano-chelated complex fertilizers also have great environmental benefits; balancing soil toxicity levels, increases solubility and absorption of microelements in soils, releasing elements fixation (phosphorus, nitrogen -ammonium and nitrates forms-, potassium, calcium and magnesium) in soils, increases nitrogen absorption, reduce and rebalance underwater table pollution, increasing or maintain viable soil microorganisms and worm populations, energy producing in rooting and fruiting, reduces plant stress by modulating the rhizosphere pH for optimal absorption of mineral, protect free-ions from leaching into water, protecting sea life from harmful nitrates, presence and/or reduction of heavy metals from soil, use of less water due to higher availability and efficient absorption of minerals, the produced chelated nano complex fertilizers can be used.

In some embodiments, two or more types of nano-chelated complexes may be obtained. The first type of chelate compound may be chelate complexes, nanocomplexes, transporters, and/or nanotransporters that can deliver an element and/or metal ion to a target. For example, calcium chelate nanocomplexes can deliver calcium to a target, such as, directly to a plant cell. The second type of chelate compound may be chelating agents, nanoagents, chelators, nanochelators, collectors, and/or nanocollectors that can trap an element and/or metal ion from a target and release it under the right conditions, such as soil pH, humidity, and temperature.

According to an advantageous embodiment, the polycarboxylic acid may be at least one acid selected from the group consisting of succinic acid ($C_4H_6O_4$), oxalic acid ($C_2H_2O_4$), malic acid ($C_4H_6O_5$), tartaric acid ($C_4H_6O_6$), citric acid ($C_6H_8O_7$), lactic acid ($C_3H_6O_3$), butanetetracarboxylic acid ($C_8H_{10}O_8$), itaconic acid ($C_5H_6O_4$) and gluconic acid ($C_6H_{12}O_7$), or mixtures thereof.

According to the invention, EDTA, EDDHHA, HEDTA, EDDHA, OTPA and the like are very preferentially excluded.

Preferably, the polycarboxylic acid may be at least one acid selected from the group consisting of malic acid ($C_4H_6O_5$), lactic acid ($C_3H_6O_3$), butanetetracarboxylic acid ($C_8H_{10}O_8$) and itaconic acid ($C_5H_6O_4$).

In the invention, the polycarboxylic acids are used for preparing the chelate complex core. In some examples, the unique blend of several polycarboxylic acid produces an environmentally friendly fertilizer with properties to increase the soil microorganism population, protect and/or stimulate earthworm populations, accumulate nutrient elements, reduce surface tension, improve mineral absorption profile; fast and increase mineral availability (root, leaf, stem and fruit) and accelerate the expansion of the elements in spraying and free-ions protection.

Preferably, the chelate complex core is consisting only of said at least one polycarboxylic acid, i.e. excluding all other organic acids, especially mono-carboxylic acids or other chelating agents known in the art, such as sulfur, seaweed, animal manure. With the sole use of at least one polycarboxylic acid, the assembled nano-chelated complexes have a higher order than their isolated components. The weak acid environment generated by the polycarboxylic acid(s), in combination with the nano particle size, provides for a robust and flexible structure that allows for interaction with the host plant and ensures a targeted delivery.

Advantageously, the relative weight percent of the polycarboxylic acid in each nano-particle may be within the range of from 15 to 40 wt%, more preferably of from 20 wt% to 35 wt%, providing the advantages above exposed.

Preferably, the particle size of the chelated complex compounds is of from 10 nm to 100 nm, more preferably of from 15 nm to 90 nm, even of from 20 to 80 nm, especially of from 30 to 80 nm.

Advantageously, the nano-chelated complexes of the invention, useful as chelate fertilizers, is solely consisting of a chelate complex core made of said polycarboxylic acid, or mixtures of polycarboxylic acids, incorporating therein said at least one first cationic compound, and further said at least a second cationic compound. The nano-chelated complexes can use the same cationic compound for both purposes for mono-element fertilizers (i.e. Nitrogen, Potassium, Zinc). The Applicant has obtained nano-chelated complexes that do not include any further compound to increase the stability thereof, i.e. EDTA, EDDHHA, HEDTA, EDDHA, OTPA and the like, various additives, such as silicon dioxide, titanium dioxide, silver oxides, catalysts, dispersants, emulsifiers, adjuvants, nano-additives, preservatives, while not impairing the technical effect thereof.

Advantageously, the weight percentage of the first cationic compound in the core chelate complex may be within the range of 5 to 35 wt%, preferably of from 5 to 30 wt%, more preferably of from 5 wt% to 25 wt%, the rest weight% being the polycarboxylic acid, providing a stable complex. The “wt%” means the weight of the first cationic compound based of the total weight of the core chelate complex.

The weight% of the second cationic compounds, that are set on the core chelate complex, are predetermined by agronomic specialists to in fact release the appropriate quantity of cationic compounds for plants. It appears that said useful released quantity, being the bioavailable (dissolved or free-ion minerals) percentage for use as fertilizer, is less than the wt% of the cationic compounds. For example, “fertilizer mixtures with 25 wt% of phosphorous” as used in agriculture, are in fact nano-chelated complexes which are prepared using 65 wt% of phosphorous source material for generating the second cationic compound, but only 25% are bioavailable, independently of the nature of core chelate complex. Another example are “fertilizer mixtures with 10 wt% of iron”, which are nano-chelated complexes prepared using 70 wt% of iron source material for generating the second cationic compound, but only 10% are bioavailable independently of the nature of core chelate complex, due to the elevated weight of the source iron carrier. For these both examples, the final nano-chelated complexes may also contain some lower wt% of other second cationic compounds.

The above mentioned advantages create nano-chelated complexes of high availability for plants, the net weight percentage of each of the second cationic compound in its soluble form respectively, i.e the bioavailable percentage, based of the total mass of each particle may be: of from 0 to 20% of N, of from 0 to 30 wt% of K, of from 0 to 25 wt% of P, of from 0 to 25 wt% of Mg, Ca and Mn, of 0 to 22 wt% of Zn, of from 0 to 15 wt% of Fe, of from 0 to 15 wt% of Cu, Se, Co, Na, Ni, Cl, I, Sr, Cr B, Si, OC and S, independently, the total weight % being different from 0.

For example, for obtaining a nano-fertilizer comprising 20 wt% of zinc, said weight% being the bioavailable percent, 5 wt% of urea (45%) is used as the first source material providing N, as the first cationic compound, 25 wt% of any polycarboxylic acid, then 65 wt% of a mixture of zinc-oxide, - sulphide, - nitrate are used.

For obtaining a nano-fertilizer comprising 10 wt% of iron, said weight% being the bioavailable percent, 5 wt% of urea (45%) is used as the first source material providing N, as first cationic compound, 25 wt% of any polycarboxylic acid, then 55 wt% of a mixture of iron-oxide, - sulphide, - nitrate are used. This specific fertilizer includes some low amounts of other compounds, such as K, Zn, Ca, Cu, Mg and Mn.

The combination of the number of elements and the bioavailable wt% of each is determined on the purpose for which the final nano-particles are designed. For example, a combination or mixture of nano-chelate compounds can be designed based of zinc (Zn – 5%), manganese (Mn – 5%) and calcium (Ca - 0.4%) for the purpose of prevention of falling fruit. Another example would be a combination of nano-compounds based on nitrogen (N - 3%), phosphorus (P - 1%), potassium (K - 1.5%), magnesium (Mg – 4%), calcium (Ca – 0.7%), iron (Fe – 2.5%), zinc (Zn – 3%), copper (Cu - 0.01%), manganese (Mn – 0.8%), boron (B - 0.06%), for the general enhancement & increase of brix and colour of tomatoes.

The nano-chelated complexes may be available as a powder or in liquid form for use in agriculture. Depending on the final formulation type (powder or liquid) of said nano-chelated complexes, the above-defined bioavailable percentage of second cationic compounds present therein may vary due different environment where the second cationic compounds are.

As an example, nano-particles of chelated complex compounds may comprise 25 wt% of a polycarboxylic acid, 10 wt% of the first cationic compound(s) and 65 wt% of the second cationic compound(s), the latter wt% not being the bioavailable percentage.

The invention also relates to a process for preparing nano-particles of chelated complex compounds of the invention, comprising the followings steps of:

a) adding a predetermined quantity of at least one polycarboxylic acid into a predetermined quantity of at least one first source material of at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof, and blending the whole, thereby forming chelate complex core compounds made of the at least one polycarboxylic acid incorporating the at least one first cationic compound therein;

b) milling and particle sizing of the core chelate complex compounds obtained in step a);

c) adding a predetermined quantity of at least one second source material of at least one second cationic compound, said second cationic compound being selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), Sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC) or mixtures thereof, to the core chelate complex compounds, and of mixing thereof, resulting in a nano-chelated complexes mixture;

d) milling and particle sizing of the mixture obtained in step c) thereby forming nano-particles of chelated complex compounds, wherein particle size thereof is ≤ 100 nm.

All advantages of the obtained nano-chelated complexes, wherein particle size thereof is ≤ 100 nm, have been previously commented.

The step a) consists in adding a predetermined quantity of at least one polycarboxylic acid into a predetermined quantity of at least one of first source compound of at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof, and blending (or mixing) the whole, thereby forming chelate complex core compounds made of the at least one polycarboxylic acid incorporating the at least one first cationic compound therein.

Before step a), the process may include an initial step of milling each of the raw materials, i.e. the at least one polycarboxylic acid, first source material(s), and second source material(s), to obtain particles presenting sizes of about 100-300 nm. Preferably, no heat or chemicals, such as aqueous solutions or various organic solvents, are used in this process step. Said step of milling is performed which all classical tools known to the one skilled in the art, such as mechanical milling devices. The raw materials are used as such whatever they are solid powder components or liquid or viscous at ambient temperature.

First source material for the first cationic compounds may be, without being limited, urea, ammonium nitrate, zinc oxide, zinc sulphide, zinc nitrate, phosphoric anhydride

(P_2O_5), triple superphosphate (TSP), di-ammonium phosphate, mono-ammonium phosphate (MAP), potassium oxide, potassium sulphide, potassium nitrate, magnesium oxide, magnesium sulphide, magnesium nitrate, iron oxide, iron sulphide, iron nitrate, calcium oxide, calcium sulphide and calcium nitrate, or mixture thereof.

Preferably, after the initial step of milling and before the step a), the process may include a step of blending the first source material(s). Said step of blending is performed which all classical tools known to the one skilled in the art.

The polycarboxylic acids may be those mentioned previously.

Preferably, step a) may use only the at least one polycarboxylic acid, i.e. excluding all other organic acids, especially mono-carboxylic acids or other chelating agents known in the art, such as sulphur, seaweed, animal manure. Advantages of the only use of said polycarboxylic acids were described previously.

Owing to step a), the first cationic compound becomes fixed into a chelate structure, thereby forming chelate complex core compounds made of the polycarboxylic acid(s) incorporating first cationic compound(s) therein. Mixture of various said complex core compounds may include said compounds with different acids and different first cationic compounds. This step a) is devoted to prepare said core chelate complex to receive multiple further first cationic compound(s) and second cationic compound(s), respectively also named macronutrients/macro-elements – micronutrients/micro-elements.

In some preferred embodiments, when the chelate complex core compounds of step a) include N or P as the first cationic compound, then step a) is carried out using as first source material a nitrogen or phosphorous source compound. The core chelate complex compounds including nitrogen or phosphorous may improve the robustness of the core chelate complex structures that allows to produce the nano-chelated complexes even more stable and efficient, compared to those obtained with other first cationic compounds.

The predetermined quantity of the at least one first source material may be selected as to achieve the desired wt% of the first cationic compound. Said quantity is generally predetermined according to some preliminary studies of agronomists for obtaining the appropriate bioavailable cation combination of the final product, which determines the wt% of the first cationic compound in the chelate complex core.

In some embodiments, the predetermined quantities in step a) may be preferentially such that the weight ratio polycarboxylic acid(s):first source material(s) is of from 2:1 to 1:3.

Step a) and the optional prior steps, i.e initial step of milling and/or step of blending the starting raw materials (polycarboxylic acid(s) and first source material(s)), may be repeated multiple times. Accordingly, said step a) may be advantageously performed repetitively until the concentrations of macronutrients are achieved and uniformly coated. The first source material(s) can be added in a step by step manner or pre-blended and added as a dry blend prior to step a).

In step a), the blending of the compounds may be carried out using the raw materials, but, upon need, a minimal amount of an aqueous solution, preferably, purified water, may be added. This may be necessary to induce the chelation reaction between the polycarboxylic acid and the first source compound (hydrolyzation of the acid(s) and ion exchange), quantity thereof being as low as possible, for example for obtaining a heavy paste.

Step b) relates to the milling and the particle sizing of said chelate complex core compounds, preferably through wet milling. This step can be repeated until the desired particle size of below 150 nm is achieved. Said particle sizes are homogenized using a mechanical milling technology, preferably fluidized bed technology.

Steps b) is followed by step c) of adding a predetermined quantity of at least one second source compound of at least one second cationic compound, said second cationic compound being selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC) or mixtures thereof, to the chelate complex core compounds, and of mixing thereof, resulting in a nano-chelated complexes mixture. Up to 17 elements (first and second cationic compounds) may be advantageously combined within each core chelate complex compound, while maintaining a stable final nano-chelated complex. Heavy metals such as lead (Pb), cadmium (Cd) and arsenic (As) may also be added within the core chelate complex compound, though these are less preferred.

Second source material(s) may be added into the chelate complex core compounds in a step-by-step approach. In this approach, a single second cationic compound is added one at a time and individually, and this is repeated for each second cationic compound until the desired combination and concentration of each second cationic compound is achieved. Second source material(s) may also be pre-blended together and added in a single step. It is more preferable to carry out step c) with metal elements (i.e. iron, zinc) be integrated first in the core chelate complex compound, followed by non-metallic (i.e. manganese, boron) elements. This process can be performed element by element or multiple elements can be added at once depending on the desired concentration and synergetic properties of the added elements.

Step c) may also include the presence of the considered polycarboxylic acids added concomitantly with the second source material(s). This allows to fix the added second cationic material(s) into the chelate complex core compound. In some embodiments, the weight ratio polycarboxylic acid(s):second source material(s) may be of from 2:1 to 1:5.

As for the first source material(s), the second source material(s) that may be used are oxides, sulphides and nitrate of each of used said materials.

In some embodiments, the weight ratio between the chelate complex core(s):second source material(s) may be of from 2:1 to 1:3.

In some circumstances, the process may include, after step c) and before step d), an addition of water and a mixing step. This may be necessary to induce the chelation reaction between the chelate complex core and the second source material (hydrolyzation of the acid(s) and ion exchange), quantity thereof being as low as possible, for example for obtaining a heavy paste.

Step d) relates to milling and the particle sizing of the mixture obtained in step c), for example through wet milling, allowing to obtain a powder of said final compound which could be wet. This step can be repeated until the desired particle size of ≤ 100 nm, of final nano-chelated complexes is achieved. Preferably, said step d) is carried out to obtain particle size of preferably 10 nm to 100 nm, more preferably of from 15 nm to 90 nm, even of from 20 to 80 nm, especially of from 30 to 80 nm. A fluidized bed device may be used.

Advantageously, steps c) and d) may be repeated multiple times until the concentration of the added second cationic compounds are achieved and uniformly coated.

After step d), the process may include, if necessary, a further step e) of drying and final particle sizing of the nano-chelated complexes. The product is processed until stable nano-chelated complexes are achieved, with particle size being lower than 100 nm. The final powder of nano-particles may then be collected and stored for future packaging operations. The final nano-chelated complexes may undergo further purification step(s) (step f) through filtration, sieving, crystallization and centrifugation with known and classical devices.

After step f), a further step describes of final particle sizing of the powder chelated complex through additional wet milling. The product is processed until a stable nano-chelated complex is achieved, with particle size being lower than 100 nm. The final powder is then collected, transferred into mixing vessels and *quantum satis* (QS) with water for storage at a correct/desired concentration.

Very advantageously, the process may carried out at temperature less than 35°C. A cooling system is then required in order to ensure that temperatures do not exceed 35°C. This assures that the minerals and elements are not denaturized or altered, providing stability of the chelate complex core compounds and the nano-chelated complexes without or with particle size less than 100 nm, thereby preventing any loss of efficiency of minerals upon agriculture use, all along the implementation of various steps of the process.

The process may be carried out without the use of EDTA, EDDHHA, HEDTA, EDDHA, OTPA and the like, and various additives selected from the group consisting of silicon dioxide, titanium dioxide, silver oxides, catalysts, dispersants, emulsifiers, adjuvants, nano-additives and preservatives.

The process can easily be carry out either at lab scale or at industrial scale using known appropriate devices, vessels and element sources, especially for milling and blending, and temperature control.

The invention also relates to a use of the nano-chelated complexes of the invention as fertilizers.

Further specific non limitative examples are given with accompanying figures, wherein,

- Figure 1 schematically depicts various steps of the process according to an embodiment of the invention,
- Figure 2 and Figure 3 depict a respective view of some nano-chelated complexes by Scanning Electronic Microscope,

1) Example 1

Figure 1 schematically depicts various steps of the process according to an embodiment of the invention.

Step 102: Initial step of milling each of the raw materials, i.e. the at least one polycarboxylic acid, the first source material(s), here macroelement(s), the second source material(s), here micro-elements, to obtain particles presenting sizes of about 100 nm-300 nm.

Step 104: blending the starting raw materials, i.e polycarboxylic acid(s) independently of first source material(s).

Steps 106-108 – step a): adding a predetermined quantity of at least one polycarboxylic acid into a predetermined quantity of at least one first source material of at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof, and mixing the whole, thereby forming a chelate complex core compounds made of polycarboxylic acids incorporating at least one first cationic compound therein. Upon need, some water could be added for promoting the chelation reaction.

Step 110: steps 106-108, step a), are repeated, upon need, for the successive chelation of various macroelements.

Step 112: Step b), relates to the milling and the particle sizing of said chelate complex core compounds, preferably through wet milling. This step can be repeated until the desired particle size of below 150 nm is achieved

Steps 114-118, step c): addition of a predetermined quantity of at least one second source compound of at least one second cationic compound, said second cationic compound being selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC) with a predetermined quantity of at one additional polycarboxylic acid, or mixtures thereof, to the chelate complex core compounds, and of mixing thereof, and further addition of water, resulting in a nano-chelated complexes mixture.

Step 120, step d), milling and particle sizing of the mixture obtained in step b) thereby forming nano-chelated complexes, wherein particle size thereof is ≤ 100 nm

Step 122: step 120, step d), is repeated multiple times until the concentration of the added second cationic compounds are achieved and uniformly coated, until the blend appears to be uniform (visual observation, powder uniformity testing).

Steps 124-126: steps e) and f), drying of the powder and final particle sizing of the powder of the nano-chelated complex. The product is processed until stable nano-chelated complexes are achieved, with particle size being lower than 100 nm. The final powder is then be collected and stored for future packaging operations. The final nano-chelated complexes undergo further purification step(s) (step f) through filtration, sieving, crystallization and centrifugation with known and classical devices.

Step 126: after step f), a further step describes of final particle sizing of the chelated complexes powder through additional wet milling. The product is processed until stable nano-chelated complexes are achieved, with particle size being lower than 100 nm. The final powder is then collected, transferred into mixing vessels and *quantum satis* (QS) with water for storage at a correct/desired concentration. Step 126 allows the preparation of the final nano-particles in liquid medium.

During the manufacturing process, several in-processs tests are performed, such as particle size distribution, pH, content uniformity, relative humidity (RH) and powder fluidity. Following the manufacturing of the nano-chelate, samples are sent to a GLP Certified Lab for final testing and generation of a Certificate of Analysis. All performed tests follow ASTM, OECD and ISO Standards. The test conducted are among others appearance, appearance in solution, density, solubility, pH, powder flowability, mineral/element concentration and heavy metal concentrations.

2) Example 2: preparation a powder of nano-chelated complexes including phosphorous as core chelate complex, iron 10 wt% (bioavailable wt%) enriched with 7 elements.

The first step is a milling step of each material separately until they are between 100 nm and 300 nm: first and second source materials and polycarboxylic acids, materials described hereunder.

The milling step is followed by an addition of phosphoric anhydride with malic acid. Gradually water is added, then the whole is mixed, until mixture looks like a heavy paste (mixture 1).

Further, triple superphosphate (TSP) with tartaric acid are added to the previous blend (mixture 1), followed by blending until mixture is uniform (mixture 2).

To mixture 2, di-ammonium phosphate with succinic acid are added, then the whole is mixed. To the blend, water is added and mixed until mixture is uniform (mixture 3).

To mixture 3, mono-ammonium phosphate with citric acid are added, then the whole is mixed, leading to the creation of the chelate complex core blend (blend 1), having phosphorous embedded in malic acid, tartaric acid, succinic acid, citric acid, used.

The previous chelate complex core blend is wet milled to provide particles size of below 150 nm.

Further, to the considered chelate complex core blend, the following compounds are added successively:

- potassium oxide, potassium sulfide and potassium nitrate with oxalic acid,
- magnesium oxide, magnesium sulfide and magnesium nitrate with lactic acid,
- calcium oxide and calcium sulfide calcium nitrate with gluconic acid,

with blending at each sub-step and wet milling to provide particles size of below 150 nm.

Obtained are chelate complex core blends (blend 2), having phosphorous, potassium, magnesium, calcium embedded in malic acid, tartaric acid, succinic acid, citric acid, oxalic acid, lactic acid and gluconic acid.

The weight ratio polycarboxylic acid(s):first source material(s) is of from 2:1 to 1:3

Blend 2 is wet milled until particle sizes are below 100 nm.

To blend 2, microelements are added (based on the second source elements): iron oxide, iron sulfide and iron nitrate with water, and then succinic acid and butanetetracarboxylic acid and oxalic acid and malic acid, then the whole is mixed leading to nano-chelated complexes including phosphorous as core chelate complex, enriched with iron 10 wt% (bioavailable wt%) (blend A).

Blend A is wet milled until particle sizes are below 100 nm.

Further, to blend A, the following compounds are added successively:

- zinc oxide, zinc sulfide and zinc nitrate with water and butanetetracarboxylic acid and tartaric acid,
- copper oxide copper sulfide and copper nitrate with itaconic acid,

with blending at each sub-step and wet milling to provide particles size of below 100 nm having 7 cationic compounds.

The weight ratio between the chelate complex core(s):second source material(s) is of from 2:1 to 1:3.

All steps are performed with controlled temperatures of between 27 to 35° C. These steps are repeated in a gradual stages until drying is complete and the target particle size is achieved.

At each stage, powder flow, moisture (RH), and temperature (27°C-35°C) are tested.

Table A

Macro-and micro-elements	Theoretical bioavailable %	Measured bioavailable %
Fe	10	[8.0 – 12]
P	4	[3.0 – 5.0]
K	2	[1.5 – 3.0]
Zn	3	[2.5 – 4.0]
Ca	3	[2.0 – 4.0]
Cu	0.5	[0.4 – 0.8]
Mg	5	[4.0 – 6.0]

Heavy metals Cd, Co, Hg, are lower than 2 ppm, Ni and Pb are lower than 27 ppm.

The bioavailable (free-ion) wt% are determined according to ASTM, OECD or ISO standard analytical methods and/or using a validated laboratory spectroscopy device (i.e. Perkin-Elmer ELAN 6000 ICP-OES).

In the case of the example mentioned above, the obtained nano-chelated complex presents:

- A dark purple crystalline powder;
- Appearance in liquid: Clear dark red liquid;
- Density : 1.1 g/cm^3 (measured using a pycnometer);
- Freely soluble (OECD-105);
- pH: 1.8 (OECD-122), Ion/pH meter.

It should be emphasized that the pH, powder flow properties, solubility and the cationic compounds concentration in polycarboxylic acids are key characteristics to determine the nano-chelated complexes stability.

Figure 2 shows the obtained nano-chelated complexes structures.

It has been demonstrated over and over that when performing the process using initial predetermined quantities of polycarboxylic acids, first and second source materials as given higher, there is a very good correlation between the expected values and those obtained by GLP Laboratory.

3) Example 3: preparation a powder of nano-chelated complexes including nitrogen as core chelate complex, enriched with Zn, Ca, Mg

The first step is a milling step of each material separately until they are between 100 nm and 300 nm: first and second source materials and polycarboxylic acids, materials described hereunder.

The milling step is followed by an addition of urea with oxalic acid. Gradually add water, then the whole is mixed, until mixture looks like a heavy paste (mixture 1).

The previous chelate complex core compounds (mixture 1) is wet milled to provide particles size of below 150 nm.

To the previous blend (mixture 1), phosphoric anhydride, triple superphosphate (TSP) di-ammonium phosphate and mono-ammonium phosphate with malic acid are added, the whole being mixed (mixture 2).

To mixture 2, potassium oxide, potassium sulfide and potassium nitrate with succinic acid are added, mix until uniform (mixture 3).

To mixture 3, magnesium oxide, magnesium sulfide and magnesium nitrate with malic acid are added, then mixed for 10 min (mixture 4).

To mixture 3, calcium oxide, calcium sulfide, calcium nitrate with tartaric acid are added, and then mixed until uniform.

The previous chelate complex core blend is wet milled to provide particles size of below 150 nm. A drying step may be included after each addition step.

Obtained are chelate complex core blends having nitrogen, phosphorous, potassium, magnesium, calcium embedded in malic acid, tartaric acid, succinic acid and oxalic acid.

Further, to the considered chelate complex core blend, the following micro-elements are added successively (based on the second source materials):

- iron oxide, iron sulfide and iron nitrate with water and then succinic acid and butanetetracarboxylic acid, then mixed until uniform.;
- zinc oxide, zinc sulfide and zinc nitrate with water and then itaconic acid and tartaric acid, then mixed until uniform;
- manganese oxide, manganese sulfide and manganese nitrate with gluconic acid, then mixed until uniform;
- copper oxide, copper sulfide and copper nitrate with lactic acid, then mixed until uniform;
- molybdenum oxide and gluconic acid, then mixed, boron oxide, then mixed until uniform.

Drying, which could be carried out after each step, and wet milling steps are performed in temperatures between 27 to 35°C. These steps are repeated in a gradual stages until drying is complete and the target particle size of less than 100 nm is achieved.

The nano-chelates complexes include 11 macro- and micro-elements.

The weight ratio between the chelate complex core(s):second source material(s) is of from 2:1 to 1:3.

At each stage, powder flow, moisture (RH), and temperature (27°C-35°C) are tested.

Table B

Macro-and micro-elements	Theoretical bioavailable%	Measured bioavailable%
Fe	4.5	[3.5 – 5.5]

N	5	[4.0 – 6.0]
K	3	[2.5 – 4.0]
Zn	8	[6.5 – 9.5]
Ca	6	[4.5 – 7.5]
Cu	0.65	[0.5 – 0.8]
Mg	6	[5.0 – 7.0]
Mn	0.8	[0.6 – 1.2]
P	3	[2.5 – 3.5]
Mo	0.1	[0.08 – 2.0]
B	0.65	[0.5 – 1.0]

Heavy metals Cd, Co, Hg, are lower than 2 ppm, Ni is lower than 100 ppm, and Pb are lower than 11 ppm.

The bioavailable (free-ion) wt% are determined according to ASTM, OECD or ISO standard analytical methods and/or using a validated laboratory spectroscopy device (i.e. Perkin-Elmer ELAN 6000 ICP-OES).

In the case of the example mentioned above, the obtained nano-chelated complex presents:

- A dark purple crystalline powder;
- Appearance in liquid: Clear dark red liquid;
- Density : 1.1 g/cm^3 (measured using a pycnometer);
- Freely soluble (OECD-105);
- pH: 1.8 (OECD-122), Ion/pH meter.

It should be emphasized that the pH, powder flow properties, solubility and the cationic compounds concentration in polycarboxylic acids are key characteristics to determine the nano-chelated complexes stability.

Figure 3 shows the obtained nano-chelated complexes structures.

It has been demonstrated over and over that when performing the process using initial predetermined quantities of polycarboxylic acids, first and second source materials as given higher, there is a very good correlation between the expected values and the GLP Laboratory obtained ones.

1) Example 4

A study was carried out to assess the effects of the foliar application of nano-fertilizers of zinc (Zn) and boron (B) of the invention on pomegranate (Punica granatum cv. Ardestani) fruit yield and quality.

A factorial experiment was conducted based on a completely randomized block design, with nine treatments and four replications per treatment. Foliar sprays of nano-Zn chelate fertiliser at three concentrations (0, 60 and 120 mg Zn L^{-1}) and nano-B chelate fertiliser (0, 3.25 and 6.5 mg B L^{-1}) were applied as a single spray before full bloom at a rate of 5.3 L $tree^{-1}$. The application of Zn and B increased the leaf concentrations of both microelements in August, reflecting the improvements in tree nutrient status. A single foliar spray with relatively low amounts of B or Zn nano-fertilizers (34 mg B $tree^{-1}$ or 636 mg Zn $tree^{-1}$, respectively) led to increases in pomegranate fruit yield, and this was mainly due to increases in the number of fruits per tree. The effect was not as large with Zn as with B. Fertilization with the highest of the two doses led to significant improvements in fruit quality, including 4.4–7.6% increases in TSS, 9.5–29.1% decreases in TA, 20.6–46.1% increases in maturity index and 0.28–0.62 pH unit increases in juice pH, whereas physical fruit characteristics were unaffected (see Tables 1-4). Changes in total sugars and total phenolic compounds were only minor, whereas the antioxidant activity and total anthocyanins were unaffected.

Table1

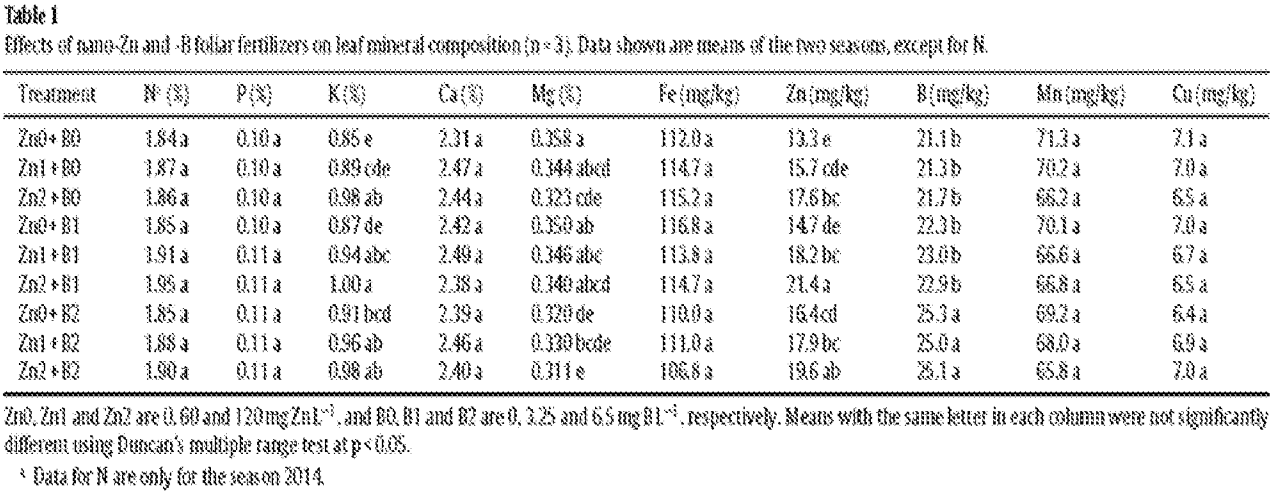


Table 1

Effects of nano-Zn and -B foliar fertilizers on leaf mineral composition (n = 3). Data shown are means of the two seasons, except for N.

Treatment	N[a] (%)	P (%)	K (%)	Ca (%)	Mg (%)	Fe (mg/kg)	Zn (mg/kg)	B (mg/kg)	Mn (mg/kg)	Cu (mg/kg)
Zn0 + B0	1.84 a	0.10 a	0.85 e	2.31 a	0.358 a	112.0 a	13.3 e	21.1 b	71.3 a	7.1 a
Zn1 + B0	1.87 a	0.10 a	0.89 cde	2.47 a	0.344 abcd	114.7 a	15.7 cde	21.3 b	70.2 a	7.0 a
Zn2 + B0	1.86 a	0.10 a	0.98 ab	2.44 a	0.323 cde	115.2 a	17.6 bc	21.7 b	66.2 a	6.5 a
Zn0 + B1	1.85 a	0.10 a	0.87 de	2.42 a	0.350 ab	116.8 a	14.7 de	22.3 b	70.1 a	7.0 a
Zn1 + B1	1.91 a	0.11 a	0.94 abc	2.49 a	0.346 abc	113.8 a	18.2 bc	23.0 b	66.6 a	6.7 a
Zn2 + B1	1.95 a	0.11 a	1.00 a	2.38 a	0.340 abcd	114.7 a	21.4 a	22.9 b	66.8 a	6.5 a
Zn0 + B2	1.85 a	0.11 a	0.91 bcd	2.39 a	0.320 de	110.0 a	16.4 cd	25.3 a	69.2 a	6.4 a
Zn1 + B2	1.88 a	0.11 a	0.96 ab	2.46 a	0.330 bcde	111.0 a	17.9 bc	25.0 a	68.0 a	6.9 a
Zn2 + B2	1.90 a	0.11 a	0.98 ab	2.40 a	0.311 e	106.8 a	19.6 ab	25.1 a	65.8 a	7.0 a

Zn0, Zn1 and Zn2 are 0, 60 and 120 mg Zn L^{-1}, and B0, B1 and B2 are 0, 3.25 and 6.5 mg B L^{-1}, respectively. Means with the same letter in each column were not significantly different using Duncan's multiple range test at $p < 0.05$.

[a] Data for N are only for the season 2014.

According to the results of this Table 1, when zinc and boron elements are used in nano form, it shows that with the use of zinc nano-chelates, the percentage of zinc element in the leaf has increased. This table also shows the improved effect of different amounts of zinc and boron on the absorption of other elements.

Table 2

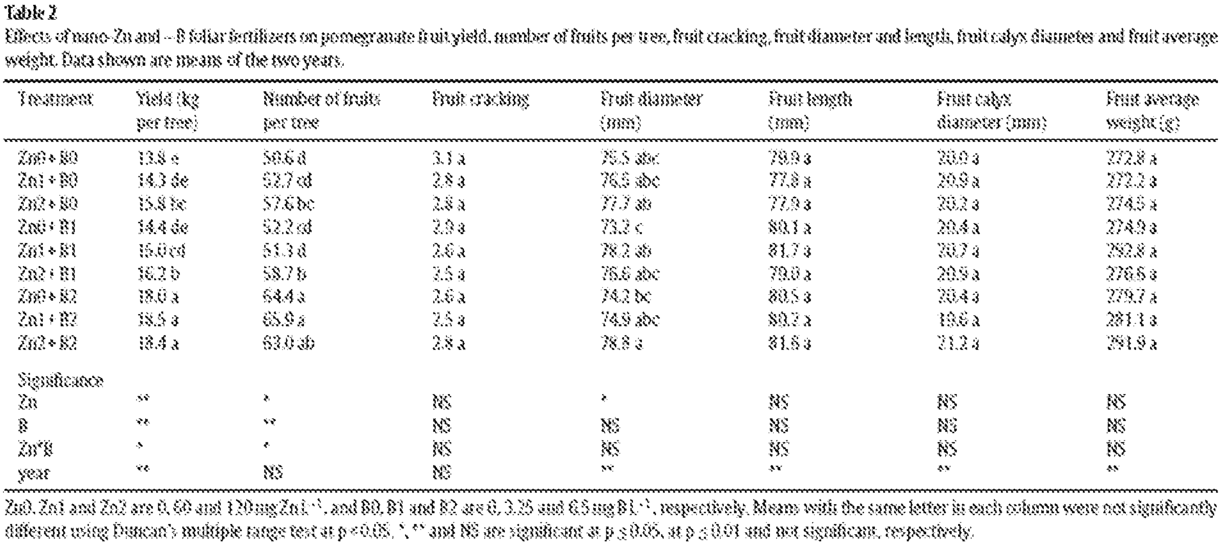


Table 2

Effects of nano-Zn and – B foliar fertilizers on pomegranate fruit yield, number of fruits per tree, fruit cracking, fruit diameter and length, fruit calyx diameter and fruit average weight. Data shown are means of the two years.

Treatment	Yield (kg per tree)	Number of fruits per tree	Fruit cracking	Fruit diameter (mm)	Fruit length (mm)	Fruit calyx diameter (mm)	Fruit average weight (g)
Zn0 + B0	13.8 e	50.6 d	3.1 a	75.5 abc	79.9 a	20.0 a	272.8 a
Zn1 + B0	14.3 de	52.7 cd	2.8 a	76.5 abc	77.8 a	20.9 a	272.2 a
Zn2 + B0	15.8 bc	57.6 bc	2.8 a	77.7 ab	77.9 a	20.2 a	274.5 a
Zn0 + B1	14.4 de	52.2 cd	2.9 a	73.2 c	80.1 a	20.4 a	274.9 a
Zn1 + B1	15.0 cd	51.3 d	2.6 a	78.2 ab	81.7 a	20.7 a	292.8 a
Zn2 + B1	16.2 b	58.7 b	3.5 a	76.6 abc	79.0 a	20.9 a	276.6 a
Zn0 + B2	18.0 a	64.4 a	2.6 a	74.2 bc	80.5 a	20.4 a	279.7 a
Zn1 + B2	18.5 a	65.9 a	2.5 a	74.9 abc	80.2 a	19.6 a	281.1 a
Zn2 + B2	18.4 a	63.0 ab	2.8 a	78.8 a	81.6 a	21.2 a	291.9 a
Significance							
Zn	**	*	NS	*	NS	NS	NS
B	**	**	NS	NS	NS	NS	NS
Zn*B	*	*	NS	NS	NS	NS	NS
year	**	NS	NS	**	**	**	**

Zn0, Zn1 and Zn2 are 0, 60 and 120 mg Zn L^{-1}, and B0, B1 and B2 are 0, 3.25 and 6.5 mg B L^{-1}, respectively. Means with the same letter in each column were not significantly different using Duncan's multiple range test at $p < 0.05$. *, ** and NS are significant at $p \le 0.05$, at $p \le 0.01$ and not significant, respectively.

According to the results of this Table 2, tree yield, number of fruits per tree and fruit cracking, foliar spraying of Zn and B fertilizers, alone or combined, increased significantly fruit yield (depending on the regimen). Both B and Zn fertilization seem to have an effect on yield, but with B the effect was more pronounced. The highest yields (18.0-18.5 kg $tree^{-1}$) were obtained with the Zn0 + B2, Zn1 + B2 and Zn2 + B2 treatments, which led to 30.4-34.0% increases when compared with the control one (13.8 kg tree^{-1}). The application of Zn and B led to significant increases in the number of fruits per tree (by 13.8–30.2%, depending on the treatments).

<u>Table 3</u>

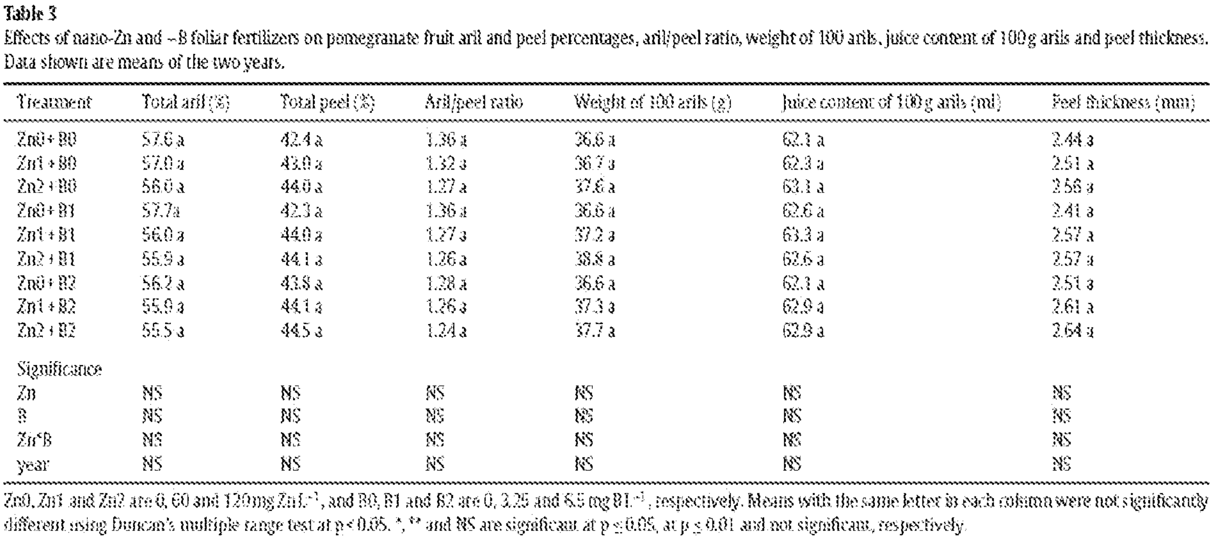


Table 3

Effects of nano-Zn and –B foliar fertilizers on pomegranate fruit aril and peel percentages, aril/peel ratio, weight of 100 arils, juice content of 100 g arils and peel thickness. Data shown are means of the two years.

Treament	Total aril (%)	Total peel (%)	Aril/peel ratio	Weight of 100 arils (g)	Juice content of 100 g arils (ml)	Peel thickness (mm)
Zn0 + B0	57.6 a	42.4 a	1.36 a	36.6 a	62.1 a	2.44 a
Zn1 + B0	57.0 a	43.0 a	1.32 a	36.7 a	62.3 a	2.51 a
Zn2 + B0	56.0 a	44.0 a	1.27 a	37.6 a	63.1 a	2.56 a
Zn0 + B1	57.7a	42.3 a	1.36 a	36.6 a	62.6 a	2.41 a
Zn1 + B1	56.0 a	44.0 a	1.27 a	37.2 a	63.3 a	2.57 a
Zn2 + B1	55.9 a	44.1 a	1.26 a	38.8 a	62.6 a	2.57 a
Zn0 + B2	56.2 a	43.8 a	1.28 a	36.6 a	62.1 a	2.51 a
Zn1 + B2	55.9 a	44.1 a	1.26 a	37.3 a	62.9 a	2.61 a
Zn2 + B2	55.5 a	44.5 a	1.24 a	37.7 a	62.9 a	2.64 a
Significance						
Zn	NS	NS	NS	NS	NS	NS
B	NS	NS	NS	NS	NS	NS
Zn*B	NS	NS	NS	NS	NS	NS
year	NS	NS	NS	NS	NS	NS

Zn0, Zn1 and Zn2 are 0, 60 and 120 mg Zn L^{-1}, and B0, B1 and B2 are 0, 3.25 and 6.5 mg B L^{-1}, respectively. Means with the same letter in each column were not significantly different using Duncan's multiple range test at $p < 0.05$. *, ** and NS are significant at $p \leq 0.05$, at $p \leq 0.01$ and not significant, respectively.

According to this table 3, zinc and boron elements have not been effective in increasing the peel thickness. Because increasing the thickness of the peel and improving it mostly linked to specialized effects of the role calcium in fruit development.

<u>Table 4</u>

Table 4

Effects of nano-Zn and -B foliar fertilizers on pomegranate fruit juice pH, TSS, TA, maturity index, total phenols, antioxidant activity, total sugars and total anthocyanins. Data shown are means of the two years.

Treatment	Juice pH	TSS (%)	TA (%)	Maturity index (TSS/TA ratio)	Total phenols (mg 100 g^{-1} FW)	Antioxidant activity (%)	Total sugars (g 100 g^{-1} FW)	Total anthocyanins (mg 100 g^{-1} FW)
Zn0 + B0	3.42 e	15.85 d	1.89 a	8.49 c	406.64 e	23.88 a	14.26 d	7.69 a
Zn1 + B0	3.55 de	15.97 d	1.81 ab	8.85 c	406.92 de	24.17 a	14.28 d	7.76 a
Zn2 + B0	3.70 cd	16.30 cd	1.59 c	10.24 b	408.09 bcde	25.72 a	14.43 bcd	8.20 a
Zn0 + B1	3.53 de	15.96 d	1.71 bc	9.43 bc	407.74 cde	24.3 a	14.37 cd	8.01 a
Zn1 + B1	3.73 c	16.26 cd	1.43 d	11.51 a	407.56 cde	24.98 a	14.54 bc	7.86 a
Zn2 + B1	4.04 a	16.96 ab	1.37 d	12.37 a	408.60 bcde	26.41 a	14.63 b	8.66 a
Zn0 + B2	3.83 bc	16.14 cd	1.39 d	11.71 a	408.77 abc	26.11 a	14.43 bcd	8.51 a
Zn1 + B2	3.99 ab	16.56 bc	1.34 d	12.34 a	409.48 ab	26.72 a	14.60 bc	8.72 a
Zn2 + B2	3.98 ab	17.06 a	1.37 d	12.41 a	409.92 a	29.48 a	14.93 a	8.68 a
Significance								
Zn	**	**	**	**	*	NS	**	NS
B	**	**	**	**	**	NS	**	NS
Zn*B	*	NS	*	*	NS	NS	NS	NS
year	NS	NS	NS	NS	NS	NS	NS	NS

Zn0, Zn1 and Zn2 are 0, 60 and 120 mg Zn L^{-1}, and B0, B1 and B2 are 0, 3.25 and 6.5 mg B L^{-1}, respectively. Means with the same letter in each column were not significantly different using Duncan's multiple range test at $p < 0.05$. *, ** and NS are significant at $p \leq 0.05$, at $p \leq 0.01$ and not significant, respectively

FW: fresh weight

According to this Table 4, Pomegranate juice pH increased significantly (by 0.28–0.62 pH units, depending on the regimen). Also, the more concentrated B and Zn within the regimen, the higher the increase of TSS in juice (4.4–7.6%), with the highest and lowest TSS values (17.06 and 15.85%, respectively) being observed in trees treated by the highest concentrations of Zn and B (Zn2 + B2) versus the untreated controls, respectively (Table 4). Regarding TA, all regimen, with the exception of Zn1 + B0, showed values lower than the controls (9.5–29.1% decreases, depending on the regimen), with the lowest one being for the treatment Zn1 + B2 (Table 4). As a result, B and Zn fertilization markedly increased the maturity index (TSS/TA ratio), by 20.6–46.1%, depending on the regimen, due to the increases in TSS and decreases in TA (Table 4). The highest increase in the maturity index was obtained in the trees sprayed with the regimen Zn2 + B2, followed by the treatments Zn2 + B1and Zn1 + B2.

The important point in the above tables (Tables 1-4) is to observe the synergistic effects of zinc and boron, in its nano-chelated form, and to use appropriate ratios during foliar application. This study demonstrates the effect of how to consume and follow the principles of nutrition in achieving the optimal effectiveness. Zinc and boron in combination synergistically improve the qualitative and quantitative properties of fruits and crops.

Example 4

Based on the studies from the experiment, it is known that the soil of the nano chelated complexes (micro fertilizers) has a high natural fertility, with a mildly alkaline/neutral reaction of soil solutions. In addition, the biologically active iron nanoparticles allow for an increase in yield capacity of some cereal crops ranging from 10- 40%. These properties indicate the soils richness in nutritional elements, thus making the nano chelated complexes favourable for crop plants. The properties of nano chelated complexes promote growth and development of plants.

Sugar Beet Plant Example

In this experiment, the Control received $N_{120}P_{90}K_{130}$ kg/ha active ingredient of mineral fertilizers during soil tillage. The latter regimen represents the normal sugar beet cultivation practices in the region. KRNV–5,6–02 cultivator was used in the inter-row spaces prior to leaf closure.

The experimental group followed a foliar application of the nano-chelated fertilizers;

Table 5. Foliar application regimen of nano-chelated fertilizers (stage, concentration, application rate) having particle sizes of less than 100 nm

Application stage	Nano fertilizers	Concentration	Application rate
1	*Nano Chelate Fertilizer Phosphorous 25%*	1 kg/400 l	2 kg/ha
	NanoChelate fertilizer Super Micro Plus	1 kg/500 l	2 kg/ha
	Nano Chelate Fertilizer Zinc 20%	1 kg/1,000 l	1 kg/ha
2	*Nano Chelate Fertilizer Potassium 23%*	1 kg/400 l	3 kg/ha
	Nano chelate Fertilizer Manganese 25%	2 kg/2,000 l	1 kg/ha
	*Nano Chelate FertilizerCopper 15%***	1 kg/1,000 l	1 kg/ha
	*NanoChelate Fertilizer Enriched Iron 10%**	1 kg/400 l	1 kg/ha
3	*Nano chelates Fertilizer Magnesium 25%*	1 kg/500 l	2 kg/ha
	Nano chelate Fertilizer Super Micro Plus	1 kg/400 l	2 kg/ha
	Nano Chelate Fertilizer Calcium 25%	2 l/1,000 l	1,000 l/ha

* The fertilizer was applied on the next day (not earlier than after 24 hours).

** The fertilizer is not mixed with the other ones in a solution, but is applied separately.

The incorporation of the nano chelate compounds (fertilizers) positively impacted the foliar nutrition and promoted the extension of photosynthetic plant mechanism functioning, as revealed through the leaf masses ability to maintain freshness and its green color for longer durations of time compared to the control groups. The use of said fertilizers increases the crop capacity of the beet plant and improved the quality, in regard to nutrients, of the said fruit. The fertilizers resulted in:

- Growth and development of plants
- Increase of sugar and beet root mass accumulation intensity
- Strengthening of root system and active gain of vegetative mass
- Improvement of plant resistance against diseases
- Increase of beet root mass and size
- Yield capacity increase up to 30.9%
- Sugar content increase in beet roots up to 7.6%
- Extension of beet root preservation period

Table 6. Productivity of sugar beets during application of the fertilizers.

Index	**Variant with nano-chelate fertilizers**	**Variant without application (Control)**
Yield capacity, t/ha	76.6	58.5
Sugar content, (overall sugar), %	18.3	17.0
Sugar content, (pure sugar), %	16.2	14.6
Sugar recovery factor (extraction)	88.52	85.88
Molasses, %	3.8	4.4
Sugar harvesting, t/ha	12.41	8.54

Conclusion:

The foliar application of nano-chelate fertilizers is effective for increasing the crop capacity and improving the quality indices of agricultural crop products because:

- *Nano Chelate Fertilizer Phosphorus 25%* increases the resistance against diseases, balances the nitrogen fertilizer effect, increases the crop yield capacity up to 9.5%; increases sugar content in beet roots up to 3.5% and sugar harvesting up to 14.8%.

- *Nano chelates fertilizer Super Micro Plus (eleven element multi nano-chelate)* promotes the accumulation of high sugar amount in beet roots, increases the resistance of plants against diseases, increases the crop yield capacity up to 6.1%; increases sugar content in beet roots up to 4.7% and sugar harvesting up to 12.7%.

- *Nano Chelate Fertilizer Zinc 20%* promotes photosynthesis and chlorophyll synthesis processes, increases the resistance of plants against diseases, increases the crop yield capacity up to 8.0%; increases sugar content in beet roots up to 2.0% and sugar harvesting up to 14.7%.

- *Nano Chelate Fertilizer Potassium 23%* promotes photosynthesis and chlorophyll synthesis processes, increases the resistance of plants against diseases, increases the crop yield capacity up to 3.4%; increases sugar content in beet roots up to 3.5% and sugar harvesting up to 7.7%.

- *Nano Chelates fertilizer Manganese 25%* makes an impact on increasing chlorophyll content, improves sugar release from leaves, increases the breathing intensity, rises water-holding capacity of tissues, reduces transpiration, promotes synthesis and sugar content increase, increases the crop yield capacity up to 8.3%; increases sugar content in beet roots up to 4.7% and sugar harvesting up to 15.8%.

- *Nano Chelate Fertilizer Copper 15%* increases resistance against fungous and bacterial diseases, improves drought and heat resistance of plants, promotes the better nitrogen absorption, synthesis and sugar content increase, increases the crop yield capacity up to 6.6%; increases sugar content in beet roots up to 5.3% and sugar harvesting up to 13.2%.

- *Nano Chelate Fertilizer Enriched Iron 10%* increases resistance against fungous and bacterial diseases, improves drought and heat resistance of plants, promotes the better nitrogen absorption, synthesis and sugar content increase, increases the crop yield capacity up to 10.6 %; increases sugar content in beet roots up to 3.5% and sugar harvesting up to 17.4%.

□ *Nano Chelate Fertilizer Magnesium 25%* increases resistance against fungous and bacterial diseases, improves drought and heat resistance of plants, promotes the better nitrogen absorption, synthesis and sugar content increase, increases the crop yield capacity up to 12.1%; increases sugar content in beet roots up to 2.3% and sugar harvesting up to 19.0%.

□ *Nano Chelate Fertilizer Calcium 25%* improves heat resistance of plants, removes toxic effect of some microelements (copper, iron and zinc), promotes the better transportation of carbohydrates and protein substances, chlorophyll synthesis, beet root growth, synthesis and sugar content increase, increases the crop yield capacity up to 5.6%; increases sugar content in beet roots up 2.0% and sugar harvesting up to 12.2%.

The combined use of fertilizers promotes the growth and development of plants; improves root system and active gaining of vegetative mass; extends the functioning of photosynthetic plant mechanism; increases the accumulation intensity of sugar, beet roots mass and size; increases the resistance of plants against diseases, the crop yield capacity up to 30.9 %, sugar content in beet roots up to 7.6% (sugar beet) and promotes the extension of beet root preservation period.

The foliar nutrition of sugar beet plantings with a combination of *Nano-chelate micro fertilizers* is effective for increasing the crop capacity and improving the quality indices of agricultural crop products, and is also effective for the representatives of a beet root group, first of all the beet botanic species (*Beta* L.), which includes the representatives of *Betacicia* and *Betacrassa* subspecies: table beets (*B.convar. Cruenfa)*; fodder beets (*B. convar.* crassa*),* sugar beets (*B.vulgarissaccharifera*), salad leaf beets (*B. convar. Vulgarly*), salad stalked beets (*B. convar. Petiolata),* decorative stalked hybrid beets (*B.convar. varioecila*).

It is possible to expect the effectiveness from applying *Nano-chelate micro fertilizers* on the other crops: carrot, radish, turnip, rutabaga, parsley, parsnip, celery.

Fertilizers will make an effective impact on the crop capacity of other agricultural crops, whose morphological structure peculiarities and development are the same as those of the beet root group, especially the representatives of the tuber crop group: such as potato, Jerusalem artichoke, yam, taro, sweet potato (batata) and manihot.

4) Example 5

Pears: Nano-chelated complexes Fertilizers vs. Control Group (without fertilizer)

A study was performed to assess the impact of the nano-chelated complex fertilizer versus the traditional farming (without the use of chemical fertilizers). The objective of the study is to determine the net impact of the nano-chelated complex fertilizers on fruit trees.

The soil was analyses prior to the study to ensure no deficiencies are present and that it can support the healthy growth/development of fruit trees. The soil assessment was the following;

INDEX	Test results
pH of salt extract, pH units	7,8
Humus substance (organic matter) %	
0-51 cm	5,1
51-90 cm	3,9
90-138 cm	2,7
138-180 cm	1,3
Nitrogen (alkalin-hydrolized), mg/kg	202,4
Mass content of Potassium mg/kg	81,9
Labile Phosphorus, mg/kg	26,5
Exchange Calcium, mmol/100g	7,2
Exchange Magnesium, mmol/100g	1,3
Carbonates, mmol/100g	0,1
Bicarbonates, mmol/100g	0,55
Mass content of Iron, mg/kg	0,07
Mass content of Manganese, mg/kg	10,04
Mass content of Copper, mg/kg	0,14
Mass content of Zink, mg/kg	0,31

The use of the nano-chelated complex fertilizer followed the regimen;

Stage	Treatment time	Fertilizer	Dosage (spraying) /1000 L	Dosage (root nutrition)	Concentration
1	Budding	Nano Chelate Fertilizer Super Micro Plus	0.5 kg	-	Concentration per 1000 liters during mixed application
		Nano Chelate Fertilizer Zinc 20%	1 kg	-	
		Nano Chelate Fertilizer Nitrogen 20%	1 liter	-	
2	Budding	Nano Chelate Fertilizer Phosphorus 25%		20 gr/ tree	
		Nano Chelate Fertilizer Potassium 23%		30 gr/ tree	
		Nano Chelate Fertilizer Nitrogen 20%		60 cc/ tree	
		Nano Chelate Fertilizer Super Micro Plus		40 gr/ tree	
3	Petals falling	Nano Chelate Fertilizer Enriched Iron 10%	1Kg		
4	Fruit setting	Nano Chelate Fertilizer Potassium 23%	1 kg	-	Concentration per 1000 liters during mixed application
		Nano Chelate Fertilizer Nitrogen 20%	1 liter	-	
5	2 weeks after stage No.4	Nano Chelate Fertilizer Copper 15%	1 kg	-	
		Nano Chelate Fertilizer Nitrogen 20%	1 liter	-	
6	2 weeks after stage No.4	Nano Chelate Fertilizer Super Micro Plus	1 kg		
		Nano Chelate Fertilizer Manganese 25%	1 kg		
7	Beginning of fruit ripeness (color change)	Nano Chelate Fertilizer Magnesium 25%	1 kg		
		Nano Chelate Fertilizer Nitrogen 20%	1 liter		
8	1 month prior to harvesting	Nano Chelate Fertilizer Calcium 25%	2 liter		

The addition of the fertilizers into the soil allowed for both the promotion of reproductive buds setting, as well as an increased amount of flowers by 13.73%. In comparison to the control group, the fertilizers revealed a quantity of 762 pcs/tree as opposed to 670 pcs/tree. The increase of flowers has resulted in increasing the loading of fruits per tree by 20.99%, exhibiting a 6.38% increase. Analyzing the size of the fruit, the weight of the pears harvested from trees treated with nano-chelate fertilizers exhibited a weight of 37-38 g at the beginning of filling, as opposed to the 20-23 g weight of the pears from the control group. In addition to the size, the average length of fruits grown with the fertilizer reached 106.3 with 81.5 mm, as opposed to the 78.3 with 66.5 mm reached on the control group. This finding proved the fertilized fruits exceeded the latter by 30.43 and 17.57%. As revealed during the picking maturity stage, the average weight of pear fruits was 154.2 g in the control group, yet the fertilized fruits showed an increase up to 196.0 g, thus exceeding the control group by 27.11%. In addition, the maximum weight of some of the fertilized fruits reached 235-299 g at the picking maturity stage.

The total output of top and first market- grade fruits can be summarized as follows;

Variant of experiment	Yield capacity		Total output of top and the first market-grade fruits, %
	kg/tree	t/ha	
Control (without fertilizers)	35.465	22.83	84.6
Nano-chelated complexes fertilizers	48.281	29.95	86.7
Gain to the check plot, %	*36.14*	*31.19*	*2.48*
HIP 0,5	*4.62*	*3.54*	-

Nano-chelated complexes Fertilizers vs. Control Group (without Fertilizer)

In addition to the increasing yield, results showed a significant increase in product quality with higher content of vitamins C and P (flavonoids) in the pear fruits, revealing an increase of 6.78% and 1.3%, respectively when compared to the control group. The sugar content of the pear fruits were higher with the fertilizers group, with an increase of 11.09% as opposed to the control. The fertilizers allowed the sugars to acids ratio to increase by 2 relative units (rel. units) and demonstrated an increase of 7.33% of soluble dry substances versus control. It was also noticed an improvement in the preservation characteristics, showing that fruits harvested with the fertilizers plots had an index of 1.37 to 1.39 times longer, when compared to control.

Through incorporating the fertilizers, the total output of top and first market- grade fruits from the pear trees reached the highest percentage of 86.7%. In comparison with the check plot, the fertilizers exhibited a 2.48% increase, as well as a decreased amount of non-standard products produced. In addition, the application of fertilizers resulted in the increase in sugar content, reaching a total of 10.62% as opposed to the 11.09% received from the control group. Exceeding the control group by 1.06%, the incorporation of the fertilizers allowed the sugars to acids ratio to increase by 2 relative units (rel.units) in the fertilization system. Through utilizing the fertilizers, results showed a significant increase in the vitamin C and P content in pear fruits, revealing an increase of 6.78 and 1.3% accordingly from the control group.

Claims

1. Nano-particles of chelated complex compounds useful as chelate fertilizers, each said compound comprising:

   a chelate complex core made of at least one polycarboxylic acid incorporating therein:

- at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof, said chelate complex core further comprising
- at least one second cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC), or mixtures thereof, forming nano-chelated complexes compounds,

   wherein the particle size thereof is ≤ 100 nm.

2. Nano-particles of chelated complex compounds according to claim 1, wherein the polycarboxylic acid is at least one acid selected from the group consisting of succinic acid ($C_4H_6O_4$), oxalic acid ($C_2H_2O_4$), malic acid ($C_4H_6O_5$), tartaric acid ($C_4H_6O_6$), citric acid ($C_6H_8O_7$), lactic acid ($C_3H_6O_3$), butanetetracarboxylic acid ($C_8H_{10}O_8$), itaconic acid ($C_5H_6O_4$) and gluconic acid ($C_6H_{12}O_7$), or mixtures thereof.

3. Nano-particles of chelated complex compounds according to claim 2, wherein the chelate complex core is consisting only of said at least one polycarboxylic acid.

4. Nano-particles of chelated complex compounds according to any of claims 1 to 3, wherein the relative weight percent of the polycarboxylic acid in each nano-particle is within the range of from 15 to 40 wt%, more preferably of from 25 wt% to 35 wt%.

5. Nano-particles of chelated complex compounds according to any of claims 1 to 4, wherein the particle size of the chelated complex compounds is of from 10 nm to 100 nm, more preferably of from 15 nm to 90 nm, even of from 20 to 80 nm, especially of from 30 to 80 nm.

6. Nano-particles of chelated complex compounds according to any of claims 1 to 5, wherein the weight percentage of the first cationic compound in the core chelate complex is within the range of 5 to 35 wt%, preferably of from 5 to 30 wt%, more preferably of from 5 wt% to 25 wt%, the rest weight% being the polycarboxylic acid, wt% being the weight of the first cationic compound based of the total weight of the core chelate complex.

7. Nano-particles of chelated complex compounds according to any of claims 1 to 5, wherein the net weight percentage of each of the second cationic compound in its soluble form respectively, the bioavailable percentage, based of the total mass of each particle is: of from 0 to 20% of N, of from 0 to 30 wt% of K, of from 0 to 25 wt% of P, of from 0 to 25 wt% of Mg, Ca and Mn, of 0 to 22 wt% of Zn, of from 0 to 15 wt% of Fe, of from 0 to 15 wt% of Cu, Se, Co, Na, Ni, Cl, I, Sr, Cr B, Si, OC and S, independently, the total weight % being different from 0.

8. Process for preparing nano-particles of chelated complex compounds to the invention, comprising the followings steps of:

    a) adding a predetermined quantity of at least one polycarboxylic acid into a predetermined quantity of at least one first source material of at least one first cationic compound selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn) and iron (Fe), or mixtures thereof, and blending the whole, thereby forming chelate complex core compounds made of the at least one polycarboxylic acid incorporating the at least one first cationic compound therein;

    b) milling and particle sizing of the core chelate complex compounds obtained in step a);

    c) adding a predetermined quantity of at least one second source material of at least one second cationic compound, said second cationic compound being selected from the group consisting of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), Sulfur (S), calcium (Ca), silicon (Si),), iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), selenium (Se), cobalt (Co), sodium (Na), nickel (Ni), chlorine (Cl), iodine (I), strontium (Sr), chromium (Cr) and organic carbon (OC) or mixtures thereof, to the core chelate complex compounds, and of mixing thereof, resulting in a nano-chelated complexes mixture;

d) milling and particle sizing of the mixture obtained in step c) thereby forming nano-particles of chelated complex compounds, wherein particle size thereof is ≤ 100 nm.

9. Process according to claim 8, wherein, before step a), the process includes an initial step of milling each of the raw materials, being the at least one polycarboxylic acid, first source material(s) and second source materials, to obtain particles presenting sizes of about 100-300 nm.

10. Process according to claim 8 or 9, wherein the first source material for the first cationic compounds is urea, ammonium nitrate, zinc oxide, zinc sulphide, zinc nitrate, phosphoric anhydride (P_2O_5), triple superphosphate (TSP), di-ammonium phosphate, mono-ammonium phosphate (MAP), potassium oxide, potassium sulphide, potassium nitrate, magnesium oxide, magnesium sulphide, magnesium nitrate, iron oxide, iron sulphide, iron nitrate, calcium oxide, calcium sulphide and calcium nitrate, or mixture thereof.

11. Process according to any of claims 8 to 10, wherein the weight ratio polycarboxylic acid(s):first source material(s) is of from 2:1 to 1:3.

12. Process according to any of claims 8 to 11, wherein step a) is repeated multiple times.

13. Process according to any of claims 8 to 12, wherein step c) further includes the presence of said polycarboxylic acids added concomitantly with the second source materials, the weight ratio polycarboxylic acid(s):second source material(s) being of from 2:1 to 1:5.

14. Process according to any of claims 8 to 13, wherein the weight ratio between the chelate complex core(s):second source material(s) is of from 2:1 to 1:3.

15. Process according to any of claims 8 to 14, wherein the process includes, after step c) and before step d), an addition of water and a mixing step.

16. Process according to any of claims 8 to 15, wherein, after step d), the process includes a further step e) of drying and final particle sizing of the nano-chelated complexes.

17. Process according to any of claims 8 to 16, wherein the nano-chelated complexes undergo further purification step(s), step f), through filtration, sieving, crystallization and centrifugation.

18. Process according to any of claims 8 to 17, wherein, after step f), a further step consist of final particle sizing of the nano-chelated complexes through additional wet milling.

19. Process according to any of claims 8 to 18, wherein the process is carried out at temperatures not higher than 35°C.

20. Process according to any of claims 8 to 19, wherein the process is carried out without the use of EDTA, EDDHHA, HEDTA, EDDHA, OTPA and the like, and various additives selected from the group consisting of silicon dioxide, titanium dioxide, silver oxides, catalysts, dispersants, emulsifiers, adjuvants, nano-additives and preservatives.

Revendications :

1. Nanoparticules de composés complexés de chélate utiles comme engrais de chélates, chacun desdits composés comprenant :

un noyau complexé de chélate constitué d'au moins un acide polycarboxylique y incorporant:

- au moins un premier composé cationique choisi dans le groupe constitué par l'azote (N), le phosphore (P), le potassium (K), le magnésium (Mg), le calcium (Ca), le zinc (Zn) et le fer (Fe), ou leurs mélanges, ledit noyau complexé de chélate comprenant en outre

- au moins un second composé cationique choisi dans le groupe constitué par l'azote (N), le phosphore (P), le potassium (K), le magnésium (Mg), le soufre (S), le calcium (Ca), le silicium (Si), le fer (Fe), le zinc (Zn), le manganèse (Mn), le cuivre (Cu), le bore (B), le molybdène (Mo), le sélénium (Se), le cobalt (Co), le sodium (Na), le nickel (Ni), le chlore (Cl), l'iode (I), le strontium (Sr), le chrome (Cr) et le carbone organique (OC), ou leurs mélanges, formant des composés de complexes nano-chélatés,

dans lesquelles la taille particulaire de ceux-ci est ≤ 100 nm.

2. Nano-particules de composés complexés de chélate selon la revendication 1, dans lesquelles l'acide polycarboxylique est au moins un acide choisi dans le groupe constitué par l'acide succinique ($C_4H_6O_4$), l'acide oxalique ($C_2H_2O_4$), l'acide malique ($C_4H_6O_5$), l'acide tartrique ($C_4H_6O_6$), acide citrique ($C_6H_8O_7$), acide lactique ($C_3H_6O_3$), l'acide butanetétracarboxylique ($C_8H_{10}O_8$), l'acide itaconique ($C_5H_6O_4$) et l'acide gluconique ($C_6H_{12}O_7$), ou leurs mélanges.

3. Nano-particules de composés complexés de chélate selon la revendication 2, dans lesquelles le noyau complexé de chélate est constitué uniquement dudit au moins un acide polycarboxylique.

4. Nano-particules de composés complexés de chélate selon l'une quelconque des revendications 1 à 3, dans lesquelles le pourcentage en poids relatif de l'acide polycarboxylique dans chaque nano-particule se situe dans la plage de 15 à 40 % en poids, plus préférablement de 25 % en poids à 35 % en poids.

5. Nano-particules de composés complexés de chélate selon l'une quelconque des revendications 1 à 4, dans lesquelles la taille particulaire des composés complexés de chélates est de 10 nm à 100 nm, plus préférentiellement de 15 nm à 90 nm, voire de 20 à 80 nm, notamment de 30 à 80 nm.

6. Nano-particules de composés complexés de chélate selon l'une quelconque des revendications 1 à 5, dans lesquelles le pourcentage en poids du premier composé cationique dans le noyau complexé de chélate se situe dans la plage de 5 à 35 % en poids, de préférence de 5 % en poids à 30 % en poid, plus préférablement de 5 % en poids à 25 % en poids, le reste en poids étant l'acide polycarboxylique, le % en poids étant le poids du premier composé cationique sur la base du poids total du noyau complexé de chélate.

7. Nano-particules de composés complexés de chélate selon l'une quelconque des revendications 1 à 5, dans lesquelles le pourcentage en poids net de chacun des deuxièmes composés cationiques sous sa forme soluble, le pourcentage biodisponible, basé sur la masse totale de chaque particule, est respectivement : de 0 à 20 % en poids de N, de 0 à 30 % en poids de K, de 0 à 25 % en poids de P, de 0 à 25 % en poids de Mg, Ca et Mn, de 0 à 22 % en poids de Zn, de 0 à 15 % en poids de Fe, de 0 à 15 % en poids de Cu, Se, Co, Na, Ni, Cl, I, Sr, Cr, B, Si, OC et S, indépendamment, le % en poids total étant différent de 0.

8. Procédé de préparation de nanoparticules de composés complexés de chélate comprend les étapes suivantes :

a) d'ajout d'une quantité prédéterminée d'au moins un acide polycarboxylique dans une quantité prédéterminée d'au moins un premier matériau source d'au moins un premier composé cationique choisi dans le groupe constitué par l'azote (N), le phosphore (P), le potassium (K), le magnésium (Mg), le calcium (Ca), le zinc (Zn) et le fer (Fe), ou leurs mélanges, et de mélange du tout, formant ainsi des composés de noyau complexé de chélate constitués de l'au moins un acide polycarboxylique y incorporant le au moins un premier composé cationique;

b) de broyage et de dimensionnement particulaire des noyaux complexés de chélate obtenus à l'étape a) ;

c) d'ajout d'une quantité prédéterminée d'au moins un deuxième matériau source d'au moins un deuxième composé cationique, ledit deuxième composé cationique étant choisi dans le groupe constitué par l'azote (N), le phosphore (P), le potassium (K), le magnésium (Mg), le soufre (S), le calcium (Ca), le silicium (Si), le fer (Fe), le zinc (Zn), le manganèse (Mn), le cuivre (Cu), le bore (B), le molybdène (Mo), le sélénium (Se), le cobalt (Co), le sodium (Na), le nickel (Ni), le chlore (Cl), l'iode (I), le strontium (Sr), le chrome (Cr) et le carbone organique (OC) ou leurs mélanges, aux composés de noyau complexé de chélate, et de leur mélange, aboutissant à un mélange de complexes nano-chélatés ;

d) de broyage et dimensionnement particulaire du mélange obtenu à l'étape c) formant ainsi les nanoparticules de composés complexés de chélate, la taille particulaire de ceux-ci étant $\leq$ 100 nm.

9. Procédé selon la revendication 8, dans lequel, avant l'étape a), le procédé comprend une étape initiale de broyage de chacune des matières premières, à savoir l'au moins un acide polycarboxylique, le(s) premier(s) matériau(x) source(s) et les deuxièmes matériaux source, pour obtenir des particules présentant des tailles d'environ 100-300 nm.

10. Procédé selon la revendication 8 ou 9, dans lequel la première matière source pour les premiers composés cationiques est l'urée, le nitrate d'ammonium, l'oxyde de zinc, le sulfure de zinc, le nitrate de zinc, l'anhydride phosphorique (P_2O), le triple superphosphate (TSP), le di-ammonium phosphate, le mono-ammonium phosphate (MAP), l'oxyde de potassium, le sulfure de potassium, le nitrate de potassium, l'oxyde de magnésium, le sulfure de magnésium, le nitrate de magnésium, l'oxyde de fer, le sulfure de fer, le nitrate de fer, l'oxyde de calcium, le sulfure de calcium et le nitrate de calcium, ou un mélange de ceux-ci.

11. Procédé selon l'une quelconque des revendications 8 à 10, dans lequel le rapport pondéral acide(s) polycarboxylique(s):premier(s) matériau(x) source(s) est de 2:1 à 1:3.

12. Procédé selon l'une quelconque des revendications 8 à 11, dans lequel l'étape a) est répétée plusieurs fois.

13. Procédé selon l'une quelconque des revendications 8 à 12, dans lequel l'étape c) comprend en outre la présence desdits acides polycarboxyliques ajoutés concomitamment avec les deuxièmes matériaux sources, le rapport pondéral acide(s) polycarboxylique(s):deuxième(s) matériau(x) source(s) étant compris entre 2:1 à 1:5.

14. Procédé selon l'une quelconque des revendications 8 à 13, dans lequel le rapport pondéral entre le ou les noyau(x) complexé(s) de chélate:deuxième(s) matériau(x) source(s) est de 2:1 à 1:3.

15. Procédé selon l'une quelconque des revendications 8 à 14, dans lequel le procédé comprend, après l'étape c) et avant l'étape d), une addition d'eau et une étape de mélange.

16. Procédé selon l'une quelconque des revendications 8 à 15, dans lequel, après l'étape d), le procédé comprend une étape supplémentaire e) de séchage et de dimensionnement particulaire final des complexes nano-chélatés.

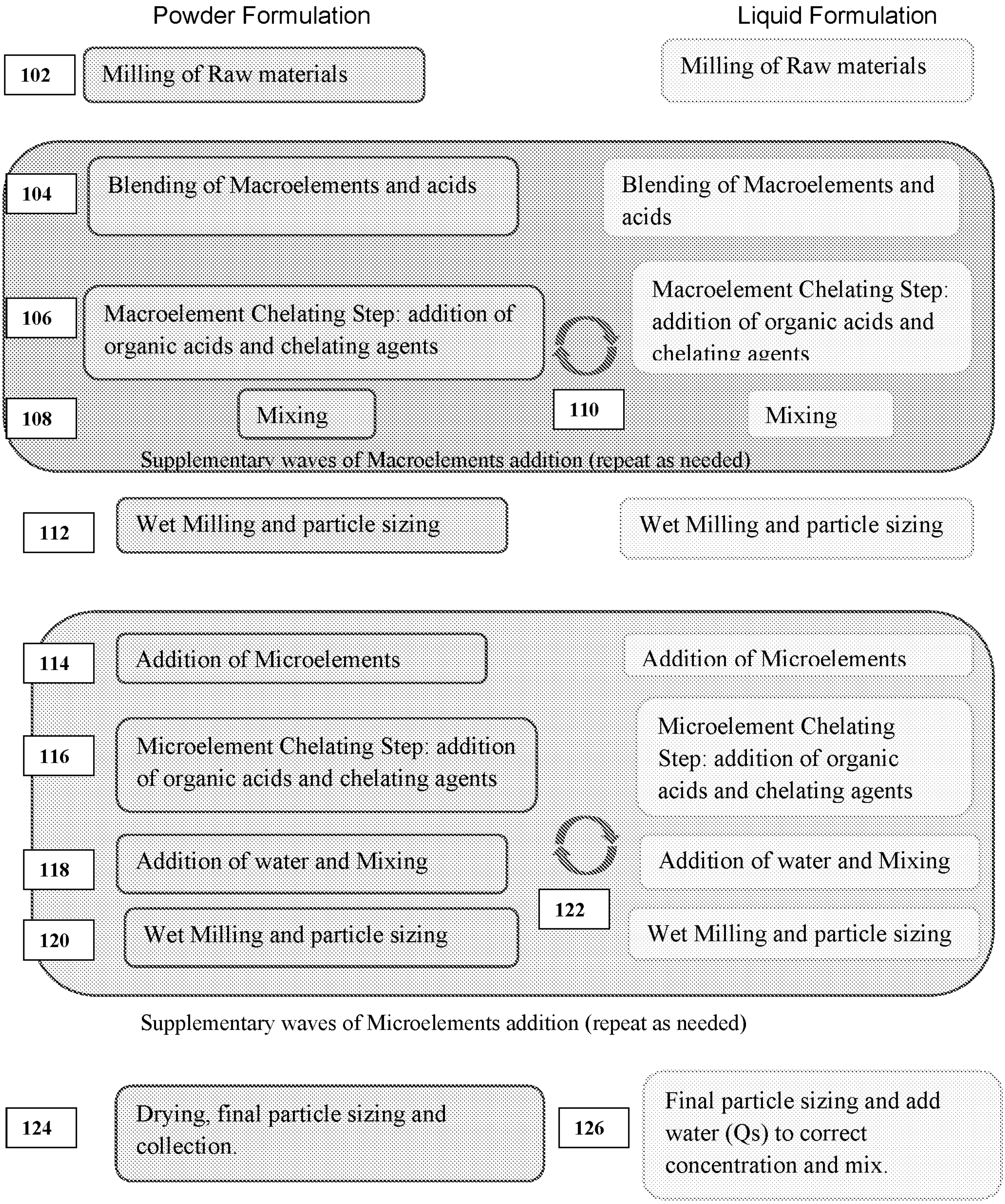
17. Procédé selon l'une quelconque des revendications 8 à 16, dans lequel les complexes nano-chélatés subissent une ou plusieurs étapes de purification supplémentaires, étape(s) f), par filtration, tamisage, cristallisation et centrifugation.

18. Procédé selon l'une quelconque des revendications 8 à 17, dans lequel, après l'étape f), une étape supplémentaire consiste en un dimensionnement final des complexes nano-chélatés par un broyage humide supplémentaire.

19. Procédé selon l'une quelconque des revendications 8 à 18, dans lequel le procédé est mis en oeuvre à des températures non supérieures à 35°C.

20. Procédé selon l'une quelconque des revendications 8 à 19, dans lequel le procédé est mis en oeuvre sans utilisation d'EDTA, EDDHHA, HEDTA, EDDHA, OTPA et similaires, et de divers additifs choisis dans le groupe constitué par le dioxyde de silicium, le dioxyde de titane, oxydes d'argent, catalyseurs, dispersants, émulsifiants, adjuvants, nano-additifs et conservateurs.

Fig. 1


Powder Formulation
Liquid Formulation
102
Milling of Raw materials
Milling of Raw materials
104
Blending of Macroelements and acids
Blending of Macroelements and acids
106
Macroelement Chelating Step: addition of organic acids and chelating agents
Macroelement Chelating Step: addition of organic acids and chelating agents
108
Mixing
110
Mixing
Supplementary waves of Macroelements addition (repeat as needed)
112
Wet Milling and particle sizing
Wet Milling and particle sizing
114
Addition of Microelements
Addition of Microelements
116
Microelement Chelating Step: addition of organic acids and chelating agents
Microelement Chelating Step: addition of organic acids and chelating agents
118
Addition of water and Mixing
Addition of water and Mixing
122
120
Wet Milling and particle sizing
Wet Milling and particle sizing
Supplementary waves of Microelements addition (repeat as needed)
124
Drying, final particle sizing and collection.
126
Final particle sizing and add water (Qs) to correct concentration and mix.

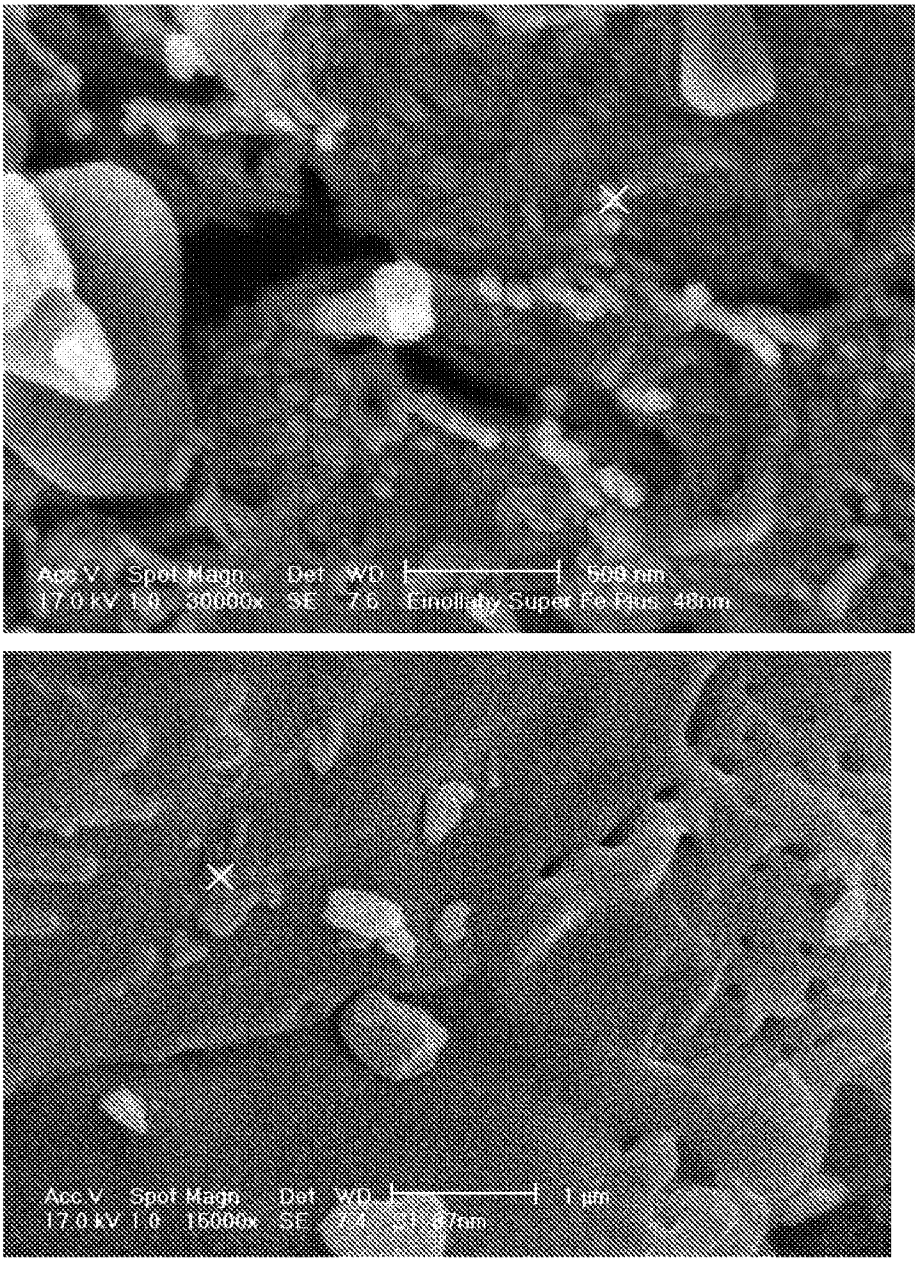

Acc.V Spot Magn Det WD 500 nm
17.0 kV 1.0 30000x SE 7.6 Einollidy Super Fe Plus 48nm
Acc.V Spot Magn Det WD 1 µm
17.0 kV 1.0 15000x SE 7.4 S1 47nm

Fig. 2

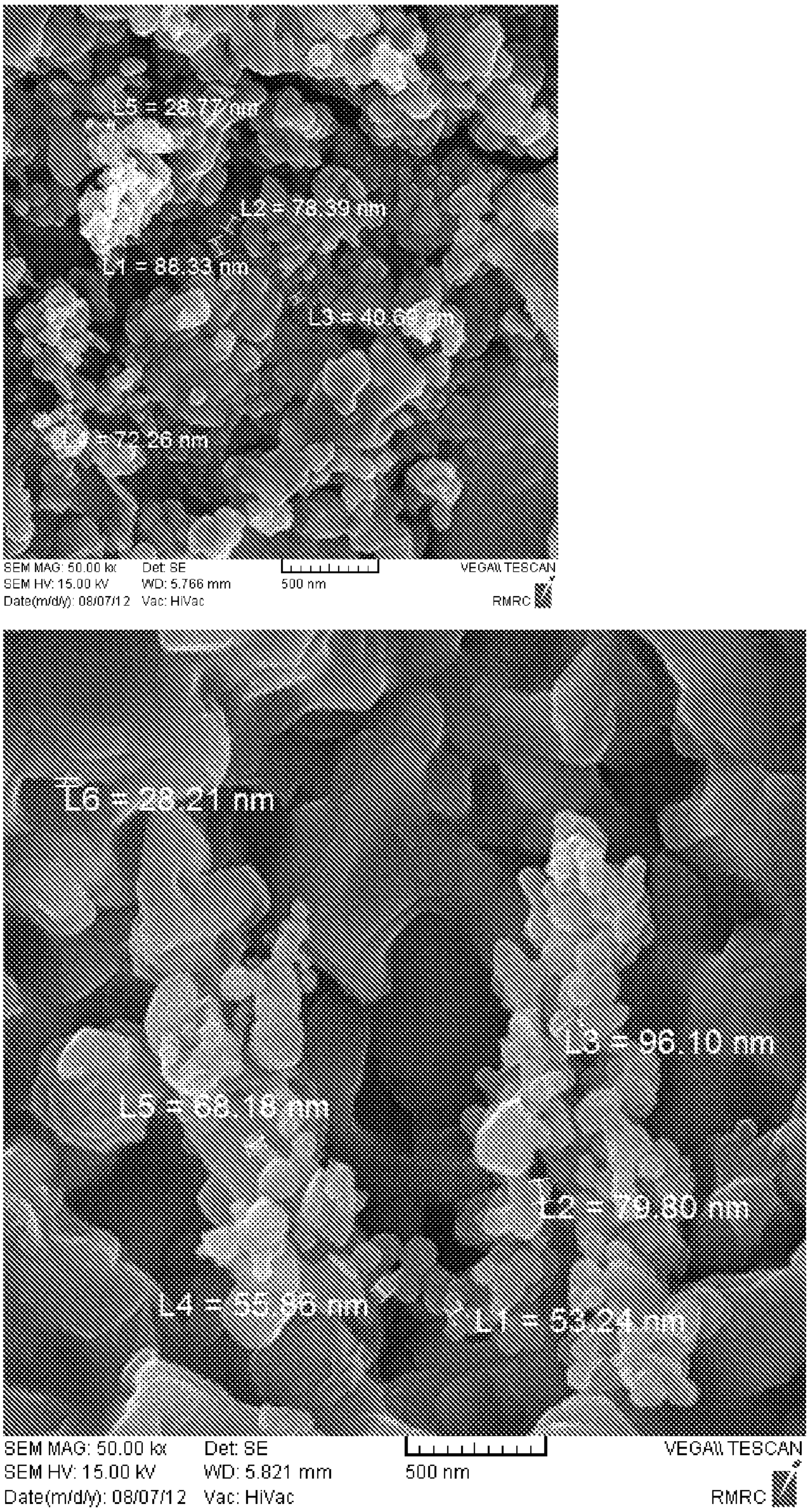

L5 = 28.72 nm
L2 = 78.39 nm
L1 = 88.33 nm
L3 = 40.6 nm
= 72.26 nm
SEM MAG: 50.00 kx
Det: SE
500 nm
VEGA\\ TESCAN
SEM HV: 15.00 kV
WD: 5.766 mm
Date(m/d/y): 08/07/12
Vac: HiVac
RMRC
L6 = 28.21 nm
L3 = 96.10 nm
L5 = 68.18 nm
L2 = 79.80 nm
L4 = 55.86 nm
L1 = 53.24 nm
SEM MAG: 50.00 kx
Det: SE
500 nm
VEGA\\ TESCAN
SEM HV: 15.00 kV
WD: 5.821 mm
Date(m/d/y): 08/07/12
Vac: HiVac
RMRC

Fig. 3