pH Stability of Fe-Chelates in Soilless Culture

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Abstract

Soilless cultures could not exist without the discovery that iron chelates can be used in nutrient solutions for delivering iron to the plant roots. The choice of the best iron chelate in soilless cultures is discussed by making use of a speciation calculation model. Fe-EDTA is often not stable enough and Fe-DTPA (or sometimes Fe-EDDHA or Fe-EDDHMA) is the product of choice. Also the need for chelation of Mn, Zn and Cu is discussed and what the influence is on the stability of the iron chelate, when the A- and B-tank solutions come together in the final nutrient solution. Also the consequences of a high Cu or Zn level (either chelated or not chelated) in the nutrient solution for the stability of the Fe-chelate will be shown. Both elevated levels of copper and zinc will result in lower concentrations of iron in the nutrient solution. Chelation of copper, zinc and manganese will result in a lower loss of iron.

INTRODUCTION: WHAT IS A CHELATE?

Chelation is absolutely essential for both human and plant life. Chelating agents are organic molecules that can bind metal ions extremely tightly in aqueous solutions. The word chelate is derived from the Greek “chela”, meaning “crab claw”. Like the claw of a crab a chelate grabs a metal ion and keeps it tightly in its grip. This causes a complete change in the properties of the metal ion in an aqueous solution. For instance, the valency of a 2^+ metal ion can be changed after chelation to a 1^- of the complex.

Stable chelates can be prepared from the 2^+ or 3^+ ions iron, manganese, zinc and copper. Calcium and magnesium can also be chelated but are less common in use. Boron and molybdenum are present in plant nutrition as (negatively charged) borates and molybdates, which makes chelation not necessary. The chelating agent most commonly used in agriculture is EDTA (EthyleneDiamine TetraAcetic acid), which is used to produce chelated micronutrients for all the main metal trace elements.

EDTA chelates are stable under acidic, neutral and alkaline conditions for almost all metals; the EDTA-based *iron* chelate, however, is only stable under acidic conditions. So, in addition to EDTA, four other chelating agents have been designed specifically for use with iron in neutral and alkaline conditions. These are DTPA (DiethyleneTriamine PentaAcetic acid), HEDTA (or HEEDTA, HydroxyEthylEthyleneDiamineTriAcetic acid), EDDHA (EthyleneDiamine Di(2-Hydroxyphenyl)Acetic acid) and EDDHMA (Ethylene Diamine Di(2-Hydroxy-Methylphenyl)Acetic acid). Figure 1 gives an indication of the pH stability of different iron chelates in an A-tank (high calcium levels from the calcium nitrate).

Chelating agents may allow precise control of the micronutrient status of the plant (Wallace, 1982). Since iron DTPA is stable under both acidic and neutral conditions it became the standard in soilless cultures worldwide, especially in Europe, with dose rates between 1 to 2 ppm, occasionally 3 ppm in the nutrient solution. In some countries Fe-EDTA is still in use, but the dose rates need to be higher due to the lower stability; often 3 to 5 ppm is given. In high pH conditions iron chelates derived from EDDHA and EDDHMA which are stable under acidic, neutral and alkaline conditions, are used. All types of iron chelates can be mixed with each other, especially the mix of (mainly) Fe-DTPA with some Fe-EDDH(M)A is popular in iron demanding crops like roses.

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HISTORY OF SOILLESS CULTURES

Chelation was discovered about 100 years ago, but it took another 50 years to understand its importance for agriculture. In the beginning of the fifties of last century it was discovered that an iron chelate could be used in plant nutrition (Jacobson, 1950). Together with the discovery that stonewool could be used as growing medium for crops in the seventies it is the foundation for the success story of soilless culture. In 1975 the first commercial growers in the Netherlands started with cucumbers on stonewool (van Doesburg, 1999), and many crops like tomatoes and roses followed.

One of the main advantages of soilless culture is that the consumption of crop protection chemicals, especially those related to soil-borne diseases, can be virtually eliminated. Additional advantages are more reliable cropping and increased yields, due to the possibility of fine-tuning all nutrient elements to the crop needs.

pH STABILITY OF FE-CHELATES IN NUTRIENT SOLUTIONS

The pH stability of different Fe-chelates (Fe-EDTA, Fe-DTPA and Fe-HEDTA) in standard nutrient solution has already been estimated in the past using speciation calculations.

The concentrations used for the standard nutrient solution were taken from the recommendations from the Applied Plant Research, Division Glasshouse Horticulture, Naaldwijk, Netherlands, for tomato using full recirculation in a closed system (de Kreij et al., 2003). The concentrations are:

[Ca] = 2.75 mM, [K] = 6.5 mM, [Mg] = 1 mM, $[NH_4]$ = 1 mM
$[NO_3]$ = 10.75 mM, $[PO_4]$ = 1.25 mM, $[SO_4]$ = 1.5 mM
[B] = 20 µM, [Cu] = 0.75 µM, [Mn] = 10 µM, [Mo] = 0.5 µM, [Fe] = [L] = 15 µM,
[Zn] = 4 µM

First the situation is evaluated that only the Fe is chelated, the Mn, Zn and Cu not.

The pH stability for all three Fe-chelates in the standard nutrient solution is shown in Figure 2. Especially the range between pH 5 and 7 is important. Often nutrient solutions are sent to the plants at pH 5.5, but the pH levels around the roots is often 6 to 6.5 with peaks to 7 and occasionally 7.5.

Loss of chelated Fe is caused by competition of subsequently Cu, Zn, Mn and Ca for the chelating agent and precipitation of the unchelated Fe as either $FePO_4.2H_2O$ ($pH < 6.5$) or amorphous $Fe(OH)_3$ ($pH > 6.5$).

Increased Fe concentration

In this scenario, the concentration of the Fe-chelate was increased to 25 µM, a situation which often will occur in practice when growers raise the input of Fe-chelates when deficiency is seen or expected. The other concentrations were kept identical to those in the standard nutrient solution. The concentrations are:

[Ca] = 2.75 mM, [K] = 6.5 mM, [Mg] = 1 mM, $[NH_4]$ = 1 mM
$[NO_3]$ = 10.75 mM, $[PO_4]$ = 1.25 mM, $[SO_4]$ = 1.5 mM
[B] = 20 µM, [Cu] = 0.75 µM, [Mn] = 10 µM, [Mo] = 0.5 µM, *[Fe] = [L] = 25 µM*,
[Zn] = 4 µM

The pH stability for all three Fe-chelates in the nutrient solution with the increased Fe concentration is shown in Figure 3. The curves for the *standard* nutrient solution are shown as thin dotted lines with the same color.

From the graph it is clear that increasing the Fe-chelate concentration does not change the general shape of the stability curves. However, all curves shift up with increasing Fe-chelate concentration, because the relative concentration of the competing metal ions (especially Cu, Zn and Mn) decreases.

Increased Cu concentration

In this scenario, the concentration of (unchelated) Cu was increased to 7.5 µM. The other concentrations were kept identical to those in the standard nutrient solution. The concentrations are:

[Ca] = 2.75 mM, [K] = 6.5 mM, [Mg] = 1 mM, [NH_4] = 1 mM
[NO_3] = 10.75 mM, [PO_4] = 1.25 mM, [SO_4] = 1.5 mM
[B] = 20 µM, *[Cu] = 7.5 µM*, [Mn] = 10 µM, [Mo] = 0.5 µM, [Fe] = [L] = 15 µM,
[Zn] = 4 µM

The pH stability for all three Fe-chelates in the nutrient solution with the increased Cu concentration is shown in Figure 4. The curves for the standard nutrient solution are shown as thin dotted lines with the same color.

The increased Cu concentration, which equals 50% of the Fe concentration in this case, causes more Fe to be lost from solution for all Fe-chelates than is the case for the standard nutrient solution. It is observed that at low pH (below 4.25), more Fe is lost from DTPA than from EDTA. This is caused by the formation of H-Cu-DTPA and Cu_2-DTPA complexes. However, at higher pH (above 4.25) DTPA keeps more Fe in solution than EDTA. Over the whole pH range, HEDTA is least able to keep Fe in solution against the competition of Cu.

Increased Zn concentration

In this scenario, the concentration of Zn was increased to 12 µM. This high zinc level can occur in practice when water is collected via zinc gutters or when high zinc sulphate dosages are used. The other concentrations were kept identical to those in the standard nutrient solution. The concentrations are:

[Ca] = 2.75 mM, [K] = 6.5 mM, [Mg] = 1 mM, [NH_4] = 1 mM
[NO_3] = 10.75 mM, [PO_4] = 1.25 mM, [SO_4] = 1.5 mM
[B] = 20 µM, [Cu] = 0.75 µM, [Mn] = 10 µM, [Mo] = 0.5 µM, [Fe] = [L] = 15 µM,
[Zn] = 12 µM

The pH stability for all three Fe-chelates in the nutrient solution with the increased Zn concentration is shown in Figure 5. The curves for the standard nutrient solution are shown as thin dotted lines with the same color.

The increased Zn concentration, which equals 80% of the Fe concentration in this case, causes more Fe to be lost from solution for all Fe-chelates than is the case for the standard nutrient solution. For all Fe-chelates, the increased loss of Fe starts at a higher pH than was observed in case of the increased Cu concentration, which is due to the lower stability of Zn-chelates compared to Cu-chelates.

The huge losses of iron due to the high zinc concentrations explain why zinc can cause enormous problems with Fe uptake and deteriorate plants, like the example in Kaminsky and Scharpf (1991): 34 µM Zn caused lower rose yield and root area, while 126 µM Zn showed severe Fe-deficiency chlorosis in aeroponics.

THE EFFECT OF ALSO CHELATING MN, ZN AND CU IN NUTRIENT SOLUTIONS ON THE IRON AVAILABILITY

The major advantage of using Mn-EDTA, Zn-EDTA and Cu-EDTA over inorganic salts of these micronutrient metals is that the iron chelate will be protected against metal exchange. Already at low pH levels respectively the copper, zinc and manganese from inorganic salts will replace the iron in the chelate. This already starts at lower pH levels than for calcium: already at a pH of 4 copper will start replacing the iron in the chelate. This is very clearly illustrated in Figure 6.

From this figure it can also be seen how this can be overcome: by using manganese-, zinc- and copper EDTA, all iron will remain chelated up to a pH of 7. If sulfates were used, almost double the quantity of iron DTPA needs to be used at this pH to avoid iron deficiency in the crops!

CONCLUSIONS

Compared to the standard nutrient solution (with Fe-DTPA and unchelated Mn, Zn and Cu):

- Increasing the Fe-chelate concentration will result in less precipitation of Fe, because the relative amount of competing metal ions (especially Cu, Zn and Mn) decreases;
- Increasing the Cu concentration will result in more precipitation of Fe. At low pH (below 4.25) Fe-DTPA is somewhat less stable than Fe-EDTA, whereas at higher pH (above 4.25) the relative stability is reversed;
- Increasing the Zn concentration will result in more precipitation of Fe, but this effect starts at higher pH values than in the case of increased Cu concentration;
- Chelating Mn, Zn and Cu will prevent large quantities of Fe precipitate due to the avoidance of competition for the chelating agent. This will result in a stable supply of Fe at all pH levels as normally observed in soilless culture systems.

ACKNOWLEDGEMENTS

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Figures

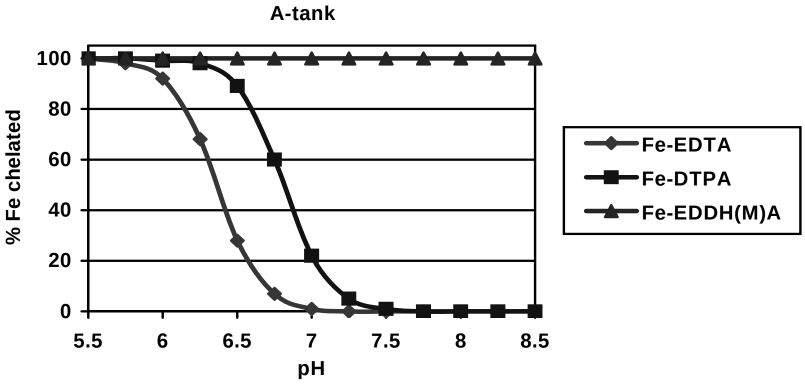

Fig. 1. pH stability of different iron chelates in an A-tank (high calcium levels from the calcium nitrate).

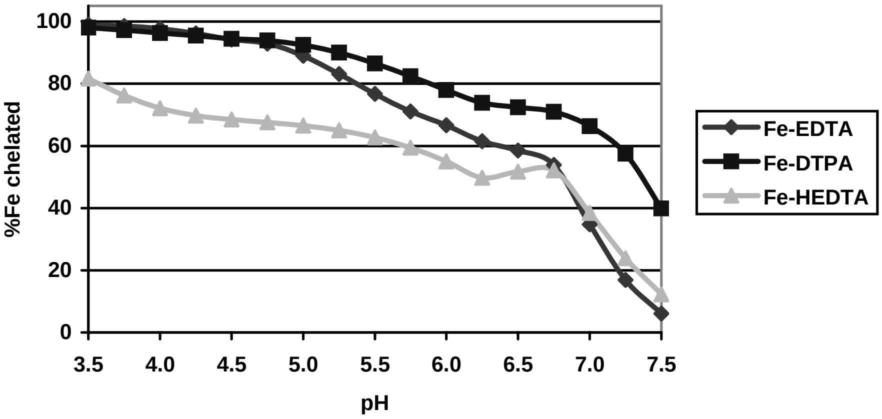

Fig. 2. pH stability of different iron chelates in the standard nutrient solution.

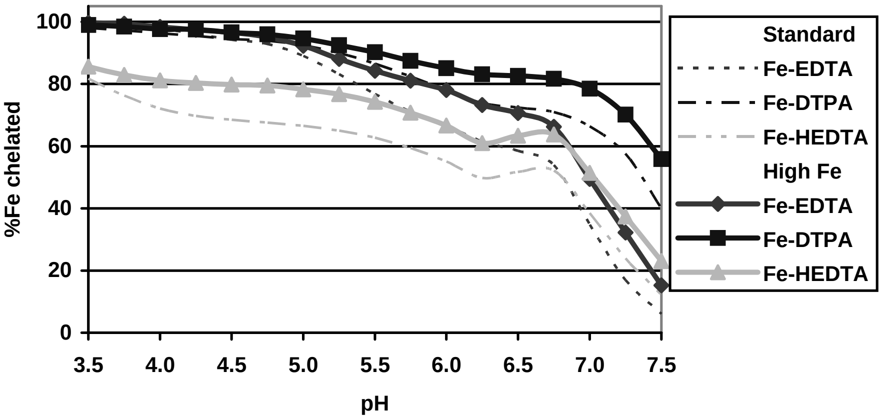

Fig. 3. pH stability of different iron chelates in nutrient solution with increased Fe concentration. The curves for the standard nutrient solution are shown as thin dotted lines with the same color.

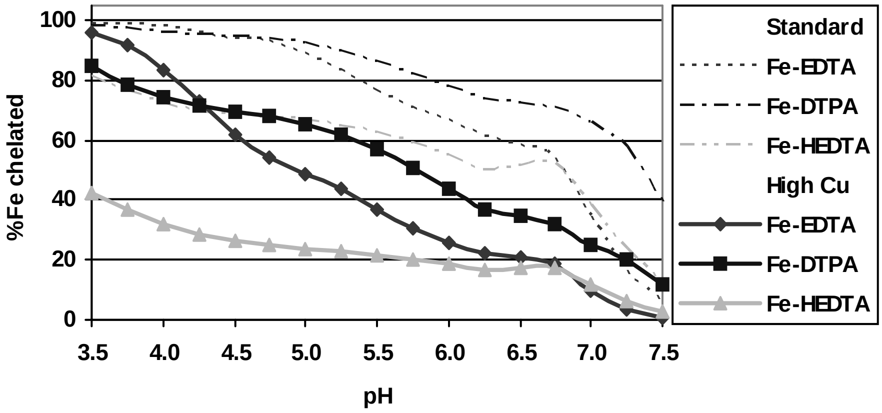

Fig. 4. pH stability of different iron chelates in nutrient solution with increased Cu concentration. The curves for the standard nutrient solution are shown as thin dotted lines with the same color.

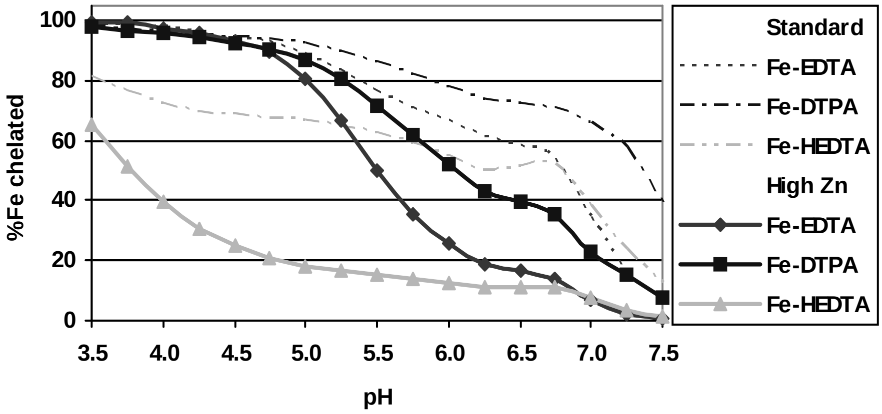

Fig. 5. pH stability of different iron chelates in nutrient solution with increased Zn concentration. The curves for the standard nutrient solution are shown as thin dotted lines with the same color.

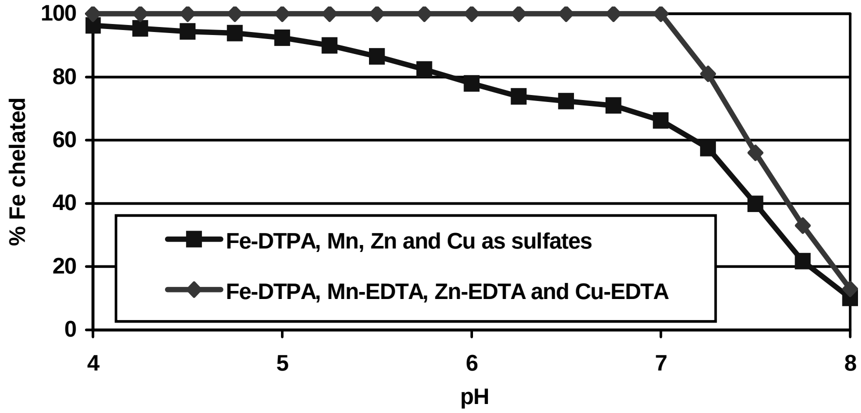

Fig. 6. The effect of chelating Mn, Zn and Cu in nutrient solutions on the iron availability.