MÖSSBAUER SPECTROSCOPIC CHARACTERIZATION OF FE-LEONARDITE COMPLEXES

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INTRODUCTION

Fe-fertilizers

synthetic Fe-chelates

- stable in wide pH range
- not degradable
- expensive
- E.g. EDTA, EDDHA, ...

natural Fe-complexes

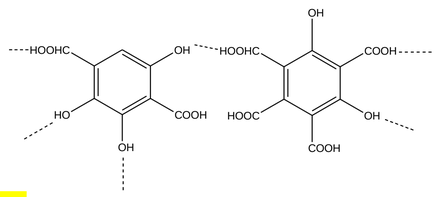
- low stabilty
- biodegradable
- cheap (by products)
- E.g. lignosulfonates (LSs), humic substances (HSs), gluconates (GL), ...

Leonardite (LN): water-soluble humic substances extracted from coal leonardite. These HSs are similar to the soil HSs, since leonardite comes from carboniferous plant species. They can be described as supramolecular associations stabilized mainly by weak forces such as dispersive hydrophobic interactions and hydrogen bonds.

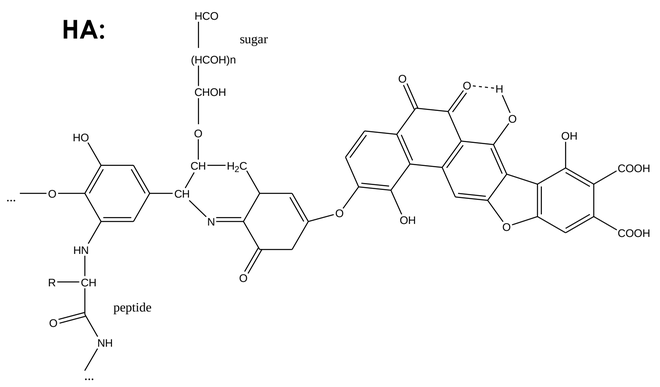
Chemical characterization of LN:

- highly oxidized state - oxygene containing functional groups, carboylic acids (FTIR, ^{13}C-NMR)
- single-ring aromatic structures, aliphatic chains
- humic acids (HA): 436 mg/kg ww, fulvic acids (FA): 130 mg/kg dw (±20)
- metals: Fe, Mn, Cu, Zn

FA:



HA:



OBJECTIVES

- study Fe^{2+}/Fe^{3+} species formed in Fe-LN complexes
- study of the effect of iron salt (Fe^{2+}/Fe^{3+}), Fe:ligand ratios and pH
- biological applications

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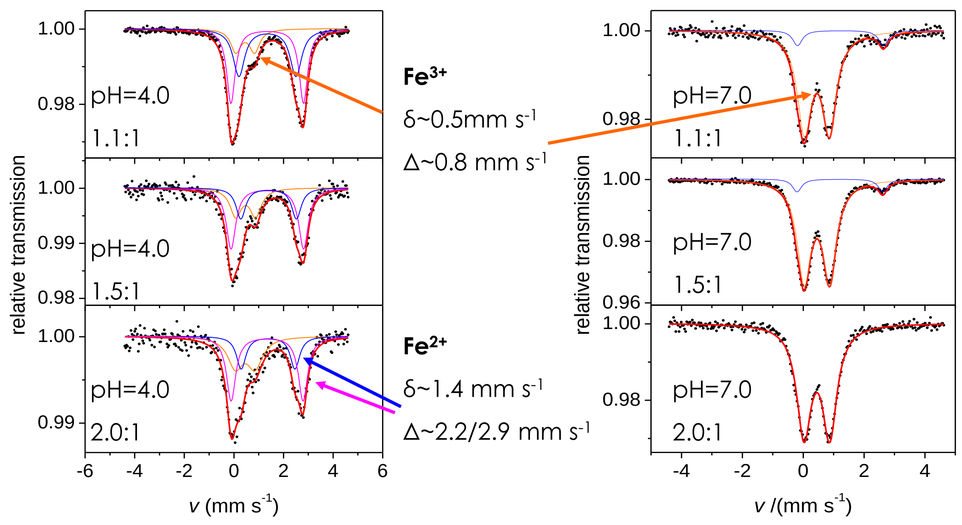
- obtain appropriate conditions for the preparation of Fe-LN complexes
- improve the stability and quality of this type of fertilizers

RESULTS AND DISCUSSION

Fe-species formed in Fe^{2+}-LS and Fe^{3+}-LS complexes:



Fe^{2+}: 83% ⟶ 10% (pH 4.0 ⟶ pH 7.0, at 1.1:1 LN:Fe)
Fe^{2+}: 83% ⟶ 67% (1.1:1 ⟶ 2:1 LN:Fe ratio, at pH 4.0)

- $Fe^{2+}{}_y$-$(H_2O)_x$-LN complex [1]
- $Fe^{2+}(H_2O)_6$ complex
- $Fe^{3+}{}_x(OH)_y(LN)_z$ complex
- $Fe^{3+}{}_x(OH)_y(H_2O)_z$ compounds

- Fe^{2+} suggested to form weak adducts/complex with LN. The resulting complex is sensitive to oxidation probably due to the oxygen content of air. The formation of amorphous ferrihydrite can be also suggested. In similar compounds, the formation of finely dispersed γ-FeOOH and/or γ-Fe_2O_3 was also found [2] while no crystalline, magnetically ordered Fe_2O_3 could be found.
- The complex formation between Fe^{3+} and LN is more favored compared to the divalent iron but only at neutral or probably at slightly alkaline pH. No reducing effect of LN was found.

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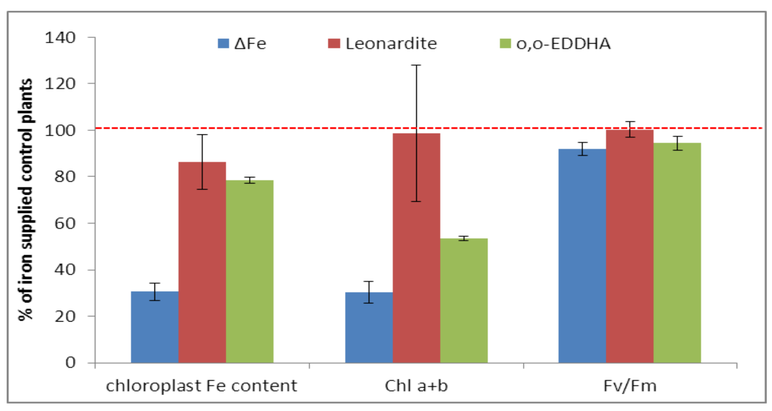
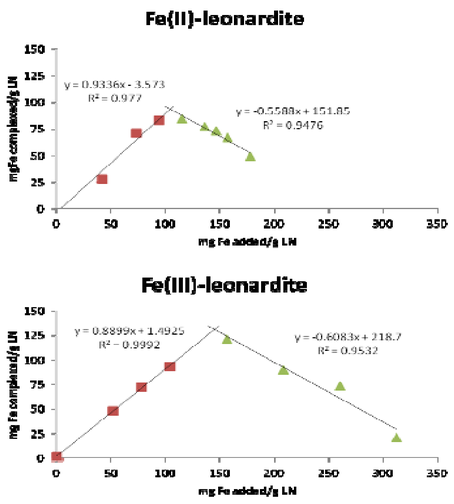
- The redox properties and the Fe-species found in the case of Fe-LN systems are very similar to those observed in the case of other natural Fe-complexes, as Fe-lignosulfonates[3] and gluconates. LN cannot prevent the oxidation of Fe^{2+} but can prevent further crystallization of Fe^{3+} oxides/hydroxides, thus, it can help to keep Fe available for plants.

Recovery of iron deficient cucumber upon Fe^{3+}-LN treatment in hydroponics:



Fe^{3+}-LN increased chloroplast iron content, total Chl content and the maximal quantum efficiency of photosystem II reaction centers (Fv/Fm, which is the main indicator of the function of the photosynthetic apparatus).

Maximum complexing capacity of LN:



- MCC with Fe^{3+}: 131±12 mg Fe/g product
- MCC with Fe^{2+}: 94 ±12 mg Fe/g product

- Fe^{3+}-LN is suggested to have higher stability at alkaline pH compared to Fe^{2+}-LN.
- The oxidation of Fe^{2+} could lead to formation of Fe-oxides/hydroxides that results in the decrease of the soluble amount of the metal.

SUMMARY AND CONCLUSION

- Since most efficient Fe-fertilizers in hydroponics are those of low stability [2, 3], as long as they are stable enough in solution, Fe^{2+}/Fe^{3+}-LN complexes are suggested to be used in hydroponics. Strong Fe^{3+}-complexes could also be used effectively in foliar treatments.
- The oxidation of Fe^{2+}-LN complexes on air has to be taken into account when applied as iron fertilizer since it may strongla influence the availability of iron in plants.
- Since no complex formation occurred between Fe^{3+} and LN at acidic pH, these compounds are suggested to be prepared and used only at neutral or at slightly alkaline pH.
- LN can prevent crystallization of Fe^{3+}-oxides or hydroxides in slightly acidic or neutral medium.
- Fe-leonardite proved to be effective in restore of chloroplast iron content and the photosynthetic apparatus. In one day of recovery treatment, both total Chl content and F_v/F_m restored completely (there was no difference between Fe supplied and Fe-leonardite treated plants), whereas o,o-EDDHA was less effective agent to improve these physiological parameters.

REFERENCES

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