STUDY OF IRON SPECIATION IN HUMIC-BASED IRON FERTILIZERS USING MÖSSBAUER SPECTROSCOPY

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A lack of bioavailable iron in soils often leads to plant disease known as iron chlorosis. Correction of iron chlorosis is usually based on application of synthetic iron (III) chelates. However, application of artificial chelates may have some negative consequences for environment and their substitution with natural organic complexing agents is very promising. Humic substances (HS) are ubiquitous in the environment and possess complexing properties against metals and favor adaptation of plants to different stress conditions.

The objectives of this work were (1) to develop humic-based iron fertilizer, (2) to study iron redox speciation in the iron humates obtained, and (3) to evaluate their efficiency as chlorosis correctors.

Iron humates were obtained using potassium humate of leonardite and iron sulfate under pH control. The commercial iron chelate Fe-EDDHA was used as a positive control. The content of iron was measured using o-phenantroline method after oxidative digestion and was 1%, 9%, and 6% in potassium humate (K-HS), iron humate (Fe-HS) and Fe-EDDHA respectively.

Biological activity under iron deficiency conditions was estimated using bioassay with cucumbers *Cucumis sativus* L. Plants were grown at the iron concentration of 25 µmol/l and HS concentration of 15 mg/l.

Iron speciation in both commercial and synthesized preparations was studied using Mössbauer spectroscopy. The acquired Mössbauer spectra are shown in Figure 1. The corresponding calculated parameters are given in Table I. Our results demonstrate that K-HS used as parent material contained both Fe(III) and Fe(II) species. The iron-enriched humate contained only Fe(III) species in two different forms: presumably, one iron form was related to the parent humate and a new form resulted from introduced iron. Fe-EDDHA also contained two forms of Fe(III), one of which (δ 0.37, Δ 0.65) was similar to the form found in humic preparations, presumably corresponding to the endogenous iron. Presence of iron species in humates similar to those seen in efficient synthetic iron chelate was interpreted as indicative of biological activity of the produced iron humate. To all appearance these parameters correspond to bioavailable ortho-ortho- complexed iron forms.

The results of bioassay have shown that treatment of cucumber plants with initial and iron-enriched humic samples resulted in an increase in chlorophyll content and root length similar to that registered for Fe-EDDHA (Table II). Of particular interest is that treatment of plants with potassium humate resulted in similar effects as both synthetic and humic iron chelates. This might be connected to the presence of endogenous iron in the initial potassium humate which turned to be highly bioavailable and have similar chemical surrounding as chelated iron. Furthermore, humic substances exhibit mitigating activity under unfavourable conditions. Hence the modification of parent material has to be directed to increasing of chelated iron in humic preparation and application of Mössbauer spectroscopy is a powerful method for evaluation of effective iron additives..

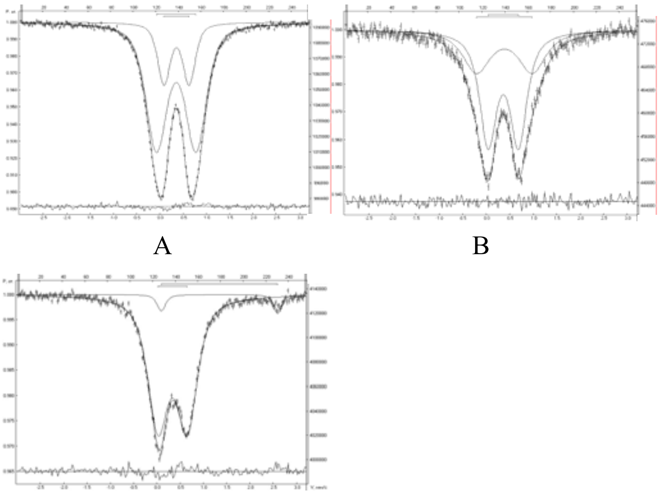
Therefore our data allow to conclude that bioavailability of iron in the synthesized chelates depends greatly on iron chemical surrounding.

Table I: Mössbauer parameters of iron preparations
(errors for δ, Δ, Γexp ±0.01 mm/s; for S ±3%; δ-relative to α-Fe)

Sample	Iron species	δ	Δ	Γ_{exp}	S, %	χ2
			mm/s			
Fe-EDDHA	Fe(III)	0.37	0.65	0.44	63	1.0
	Fe(III)	0.39	1.19	0.70	37	
Fe-HS	Fe(III)	0.35	0.54	0.32	23	1.4
	Fe(III)	0.35	0.85	0.55	77	
K-HS	Fe(III)	0.34	0.63	0.53	95	1.8
	Fe(II)	1.35	2.50	0.22	5	

Table II: Biological activity of iron additives

Sample	Chlorophyll content, mg/g	Chlorophyll content, % of blank	Root lenthg, % of blank
Blank	0.58±0.08	100±14	100±15
Fe-EDDHA	1.70±0.41	292±24	115±40
Fe-HS	1.79±0.03	308±2	205±45
K-HS	1.76±0.20	303±11	159±32



A B

C

Figure 1. Mossbauer spectra of iron chelate Fe-EEDHA (A), iron humate Fe-HS(B) and potassium humate K-HS (C). Axes : X-absorbance A,%, Y-velocity V, mm/s.