

EFFECT OF pH ON THE BEHAVIOUR OF VARIOUS IRON CHELATES IN SPHAGNUM
(MOSS) PEAT

Key words: iron chelates, pH, partition of iron, sphagnum peat

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Abstract

An incubation experiment was conducted to examine the stability and water solubility of four different iron chelates in slightly decomposed sphagnum peat as affected by pH and time of incubation.

Decrease in soluble iron upon addition of iron chelates is caused by fixation and by replacement of the chelated iron by calcium at high pH.

At low pH (pH-H₂O 4.35), recovery of soluble iron after six weeks decreases in the order: Fe-DTPA > Fe-EDTA > Fe-EDDHA > Fe-HEEDTA.

At high pH (pH - H₂O 7.25 and 7.85) this order is: Fe-EDDHA >> Fe-DTPA > Fe-HEEDTA > Fe-EDTA.

In cultivating plants at low pH, Fe-EDTA and Fe-DTPA will be the more efficient iron sources. At high pH, however, only Fe-EDDHA supplies sufficient soluble iron for a long period. Fe-HEEDTA is a poor iron source at all pH-levels because of fixation and, at high pH, substitution of calcium for iron. It was demonstrated that it is necessary to characterize commercial iron chelates by gel chromatography before testing them in plant performance studies.

INTRODUCTION

Iron chelates have mainly been tested in soils. Especially the chemical behaviour of iron chelates in calcareous soils has been studied by many workers (1, 2, 3). The findings may be explained on the basis of chelate stability and degree of fixation by clay minerals.

In The Netherlands, sphagnum peat is widely used as a growing medium for propagating plants and in substrates for pot plants. Because this organic material is acid and deficient in the principal plant nutrients, it requires liming and addition of major and minor elements. The effectiveness of iron chelates depends on the rate of decrease in water-soluble iron. This paper reports on a laboratory study of the chemical behaviour of Fe-EDTA = iron ethylenediamine tetraacetate; Fe-DTPA = iron diethylenetriamine pentaacetate; Fe-HEEDTA = iron N-hydroxyethyl ethylenediamine triacetate and Fe-EDDHA = iron ethylenediamine di(o-hydroxyphenylacetate) in sphagnum peat at four different pH-values.

EXPERIMENTAL

Characterization of the Iron Chelates

Chelate quality was assessed by gel chromatography (4). From table 1 it is clear that all iron chelates were rather pure, except one product of Fe-EDDHA (A). Only 28% of the water-soluble iron in this product was present as Fe-EDDHA.

Sphagnum Peat

The peat used was a slightly decomposed sphagnum peat, containing 94% organic matter on a dry-weight basis, with a pH-H₂O of 3.8.

Treatments

Portions of wet sphagnum peat (moisture content 88% w/w) were treated with different amounts of CaCO₃ to attain pH-values of 4.35, 5.65, 7.25 and 7.85, respectively. Samples of 90 g were given 20 mg Fe (in 50 ml of deionized water) as Fe-EDTA, Fe-HEEDTA, Fe-DTPA, pure Fe-EDDHA or impure Fe-EDDHA. The control treatment received deionized water only. All treatments were in duplicate. Samples were stored in closed jars in the dark at 20 °C. After

TABLE 1

Chemical Characteristics of the Iron Chelates used in the Incubation Experiment.

Description	Soluble iron content (%)	Purity of the iron chelates (% of soluble iron content)
Fe-EDTA	13.3	98
Fe-DTPA	9.8	100
Fe-HEEDTA	8.5	99
High-grade Fe-EDDHA	6.4	100
Low-grade Fe-EDDHA (A)	6.1	28

incubation for 1 hour, or 3, 12, 28 or 42 days, samples were taken for extraction.

Extraction Procedure

Samples of 20 g in 100 ml of deionized water were shaken in 300-ml Erlenmeyer flasks for one hour. After filtration through a folding filter (Macherey, Nagel & Co. (no 619 eh $\frac{1}{2}$)) the filtrate was clear and suitable for analysis.

Methods of Analysis

I. Soluble chelated iron. Iron in the extracts was estimated in two ways, namely:

(a) Colorimetrically. After digestion with the diacid mixture of H_2SO_4 and HNO_3 at the ratio of 1:1, iron was determined colorimetrically with o-phenanthroline (5).

(b) Spectrophotometrically. The direct ultraviolet spectrophotometric measurement according to Hill-Cottingham (6) was used. Solutions of iron chelates show a maximum absorption at a wavelength of 260 μm at which neither free chelating agents nor their calcium chelates interfere. Soluble organic substances from the peat other

than iron chelates may absorb light in the ultraviolet region. Therefore, control treatments of peat plus water were included.

II. Iron from chelates exchanged against other cations. During incubation, substitution of other cations for iron in the chelate molecule may occur depending on the stability of the iron chelate, pH and concentrations of these cations. Since CaCO_3 has been used for raising the pH, calcium will be the most important competing cation. If ferric ions are added in excess to acidified peat extracts (pH 3.0), calcium and other metal chelates are converted into iron chelates, because the stability constants of the trivalent iron chelates exceed those of any other metal.



The increase in optical density at 260 μm is then proportional to the amount of converted iron chelate (6).

Presentation of the Results

The data of soluble and exchanged chelated iron are expressed as percentages of the initially added iron. By subtracting these values from 100% the percentage of chelated iron fixed to the peat was found.

RESULTS

Table 2 shows that good agreement was obtained between both methods of analysis for soluble iron.

The nature of the chelating agent has a pronounced effect on recovery of the soluble chelated iron in the peat substrates. Fe-EDTA remains largely stable and soluble at low pH during the whole period of incubation, but at high pH soluble iron drops to about 50% after one hour, further decreasing rapidly with time. Losses in soluble iron from Fe-DTPA are small at low pH. Although recoveries of soluble iron from Fe-DTPA at high pH are much larger than those from Fe-EDTA, there is a considerable loss of soluble iron after six weeks.

TABLE 2

Percentage Recoveries of Different Iron Chelates in Peat as Affected by pH and Time of Incubation

Iron chelate	Incuba- tion time	Soluble chelated iron (% of total added iron)							
		pH 4.35		pH 5.65		pH 7.25		pH 7.85	
		C*	UV**	C	UV	C	UV	C	UV
Fe-EDTA	1h	95.9	93.2	89.5	91.2	50.6	49.2	48.1	45.0
	3d	97.8	97.3	90.4	92.7	10.5	10.3	5.3	4.9
	12d	96.3	95.0	93.6	93.1	5.5	0	1.7	0
	28d	96.5	95.9	93.8	92.3	0	0	0.2	0
	42d	94.8	94.4	91.3	91.1	0	0	0.4	0
Fe-DTPA	1h	98.6	99.0	100.2	100.0	84.3	84.9	84.3	86.7
	3d	99.9	97.2	99.0	94.9	54.8	50.3	52.7	51.3
	12d	98.6	94.6	98.2	94.4	32.3	29.8	30.8	31.3
	28d	99.5	96.4	98.2	95.9	29.1	18.7	31.6	29.4
	42d	98.2	95.9	97.4	96.2	28.2	27.2	31.6	30.3
Fe-HEEDTA	1h	80.3	80.1	81.1	80.2	41.1	43.1	40.9	41.0
	3d	75.7	76.5	68.7	67.3	12.6	13.6	14.8	14.2
	12d	70.0	70.5	59.2	59.3	9.7	11.1	12.6	12.7
	28d	62.4	61.7	50.4	53.0	10.5	11.5	11.2	9.4
	42d	51.6	51.6	37.9	38.4	10.3	10.1	10.1	9.4
Fe-EDDHA (pure)	1h	90.2	90.2	99.1	97.3	101.8	101.1	100.7	98.6
	3d	80.7	80.8	88.5	90.3	98.2	99.6	98.6	97.8
	12d	77.8	76.5	91.0	89.4	96.5	98.1	96.5	96.2
	28d	73.3	70.7	89.6	88.6	92.3	92.9	94.4	93.9
	42d	65.6	66.2	86.2	86.8	92.7	92.9	95.5	95.8
Fe-EDDHA (impure)	1h	23.6	-	24.9	-	30.8	-	35.4	-
	3d	13.5	-	16.9	-	20.2	-	24.0	-
	12d	8.4	-	11.4	-	15.2	-	16.4	-
	28d	5.5	-	7.6	-	11.0	-	10.5	-
	42d	4.2	-	5.7	-	8.0	-	9.7	-

* C = colorimetric method; ** UV = UV method

As compared with Fe-EDTA and Fe-DTPA, recovery of soluble iron from Fe-HEEDTA at low pH is much lower. At high pH there is a very rapid decrease in soluble iron at first, but after twelve days the recovery reaches a nearly constant value of about 10%. In an acid medium (pH 4.35) the recovery of soluble iron from Fe-EDDHA decreases

with time to about 66%, while at high pH practically no losses occur throughout the experiment.

Impure Fe-EDDHA differs strongly from pure Fe-EDDHA and is useless in maintaining a high level of soluble iron in the peat substrate.

The losses of soluble iron are caused by two processes, namely fixation of iron chelate by peat, and substitution of calcium for chelated iron with subsequent precipitation of the iron. This latter process occurs at high pH, when one OH-group is bound to the iron chelate. As hydroxy-iron chelates are much less stable than iron chelates, iron may be replaced by calcium depending on their stabilities. The partition of the chelated iron over the three fractions (soluble iron, exchanged iron and fixed iron) is illustrated in figure 1 for different incubation times. At each pH, fixation of Fe-EDTA and Fe-DTPA is small. The rapid decrease in soluble iron from Fe-EDTA and Fe-DTPA at high pH must be attributed to replacement of chelated iron by calcium. Especially at low pH, fixation of Fe-HEEDTA is high. At high pH, replacement of iron by calcium is the dominant process.

As would be expected, no displacement of iron from Fe-EDDHA occurs at high pH. However, it is rather surprising that at pH 4.35 one third of the added Fe-EDDHA is fixed after six weeks. Exchanged iron could not be determined in the treatments with the impure product of Fe-EDDHA as it is not known to which extent unknown organic compounds in this product contribute to the optical density at 260 μm .

DISCUSSION

As compared with the behaviour of iron chelates in soils some points of difference can be noted. In contrast with findings in soils (2, 7, 8), Fe-EDTA and Fe-DTPA are not fixed to any great extent in sphagnum peat. On the other hand, the reverse is true for Fe-EDDHA at low pH. This iron chelate, not being fixed in soils, is sorbed on the peat at pH 4.35 to a significant extent. From a viewpoint of effectiveness in supplying iron to plants in peat substrates Fe-EDTA and Fe-DTPA are better iron sources than Fe-EDDHA at low pH.

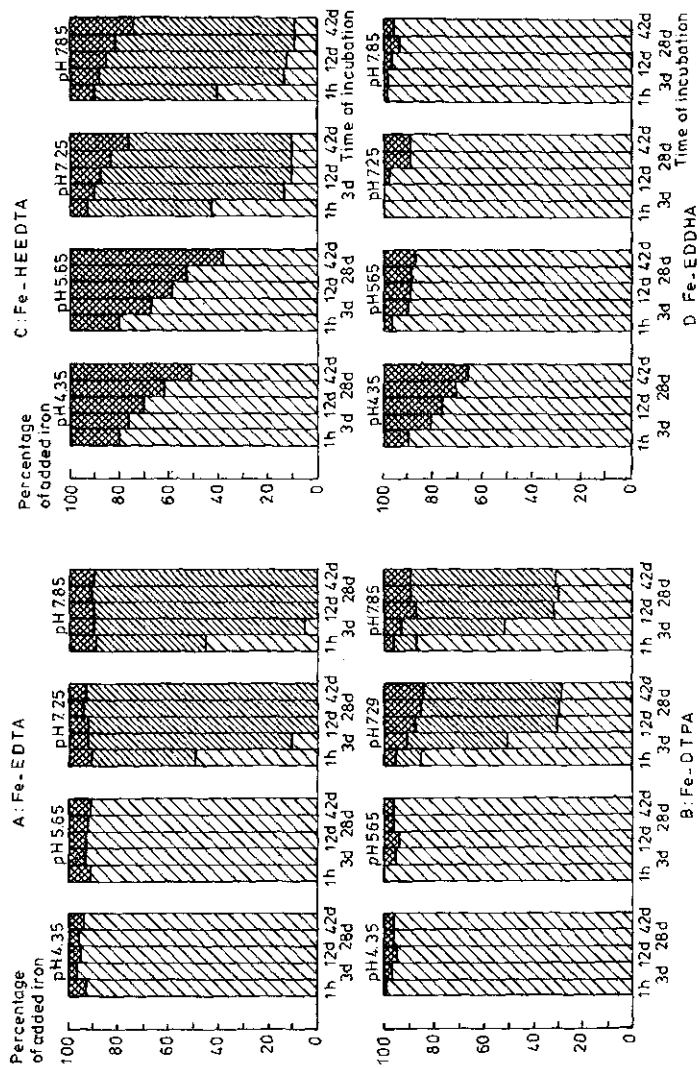


Fig. 1. Diagrammatic representation of the partition of chelated iron over three fractions (soluble iron: exchanged iron and fixed iron) as affected by pH and time of incubation of Fe-EDTA (A), Fe-DTPA (B), Fe-HEEDTA (C) and Fe-EDDHA (D).

Legends:

- soluble iron, expressed as percentage of the amount of added iron.
- exchanged iron, expressed as percentage of the amount of added iron.
- fixed iron, expressed as percentage of the amount of added iron.

Although iron chelates are biodegraded in soils and sediments (10), no microbiological degradation could be found in pure peat substrate after six weeks. The values indicating iron chelate fixation at high pH may be too high. It is possible that after replacement of chelated iron by calcium a part of the calcium chelate formed is also fixed on the peat substrate. This effect cannot be checked by the ultraviolet spectrophotometric method.

The use of Fe-HEEDTA for the control of iron deficiency on calcareous soils was proposed on the assumption that a solution of Fe-HEEDTA was more stable at high pH than a Fe-EDTA solution. This property alone is not sufficient to justify its use on peat, for the replacement of chelated iron by the large concentration of available calcium at high pH results in a rapid loss of soluble iron (Fig. 1C). Moreover, the high rate of sorption on the peat at low pH indicates that this chelate is a poor iron supplies for plants on peat substrates at all pH-levels.

From Fe-DTPA less iron remains soluble at high pH than was expected theoretically on the basis of its high stability constant. Also in this case the large losses of soluble iron are due to the replacement of chelated iron by calcium. At high pH, Fe-EDDHA is the most effective iron chelate for supplying plants with iron on peat substrates. It is clear from the results with the impure product of Fe-EDDHA that it is necessary to check the purity of the products before using them in plant performance studies (9).

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