Fe(III)−EDDHA and −EDDHMA Sorption on Ca-Montmorillonite, Ferrihydrite, and Peat

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The effectiveness of Fe chelates as Fe sources and carriers in soil can be severely limited by the adsorption of Fe chelates or chelating agents in the solid phase. To study this phenomenon, well-characterized peat, Ca-montmorillonite, and ferrihydrite were used as model compounds, and the adsorption of Fe−EDDHA and Fe−EDDHMA chelates were studied. Sorption isotherms for the meso and racemic isomers of these chelates on the soil materials are described. The variability of sorption with pH in peat and ferrihydrite was also determined because both have variable surface charge at different pH values. In montmorillonite, at low concentrations, the retention of Fe from the Fe−EDDHMA chelate is greater than the one of the Fe−EDDHA chelate. As well as the concentration increased, the inverse situation occurs. The behavior of both meso and racemic isomers of chelates in contact with Ca-montmorillonite is similar. The Fe−*meso*-EDDHA isomer was highly adsorbed on ferrihydrite, but the racemic isomer is not significantly retained by this oxide. For Fe−EDDHMA isomers, the racemic isomer was more retained by the oxide, but a small sorption of the racemic isomer was also observed. Results suggest that Fe−EDDHA chelates were more retained in peat than Fe−EDDHMA chelates. The most retained isomer of Fe−EDDHA was the meso isomer. For Fe−EDDHMA, the adsorption was very low for both racemic and meso isomers.

INTRODUCTION

Micronutrient concentration in the soil solution should be maintained at a level sufficient to supply plant requirements while minimizing leaching losses. If too little is available, plant deficiencies can occur. Since adsorption−desorption reactions tend to be faster than precipitation−dissolution processes, adsorption at solid interfaces can be a dominant factor in regulating micronutrient concentration in solution (*1*).

In Europe, the 76/116/EC directive allows chelates of the elements Fe, Mn, Cu, Zn, and Co to be used as such or incorporated in mixed fertilizers. Six chelating agents are allowed to be used for this purpose. They all belong to the group of aminocarboxylic acids and are commonly abbreviated as EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), HEEDTA (2-hydroxyethylethylenediaminetriacetic acid), EDDHA (ethylenediaminedi-(*o*-hydroxyphenylacetic) acid), EDDHMA (ethylenediaminedi-(*o*-hydroxy-*p*-methyl-phenylacetic) acid), and EDDCHA (ethylenediamine-di-(5-carboxy-2-hydroxyphenyl)acetic acid). EDDHA and EDDHMA (Figure 1) are the most used chelating agents. The aromatic ligands EDDHA and EDDHMA contain two chiral carbons. Hence, the four possible isomers are (*R*,*R*), (*R*,*S*), (*S*,*R*), and (*S*,*S*), but because of the internal symmetry of the molecules, the (*R*,*S*) and (*S*,*R*) enantiomers are the same molecule denoted as the meso isomer (Figure 1B). The (*R*,*R*) (Figure 1A) and (*S*,*S*) (not shown) enantiomers are mirror images, so they differ only in the direction of polarized light deviation. Since the affinity of the (*R*,*R*) and (*S*,*S*)
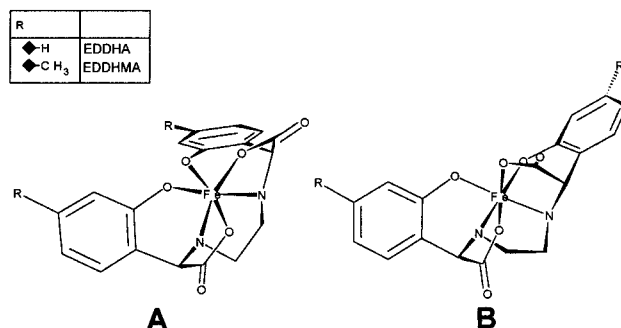
Figure 1. Spatial structure of Fe(III) chelates of *o*-EDDHA and *o*-EDDHMA (A = racemic isomer, B = meso isomer).

isomers for H⁺ or metals is the same, their separation by chemical processes has not been achieved, and generally they are called the racemic mixture.

The meso isomer of Fe−EDDHA (EDDHA^{4-} + Fe^{3+} ⇌ Fe−EDDHA^{-} log K^0 = 33.28) is less stable than the racemic isomer (log K^0 = 35.54) (*2*). For the Fe−EDDHMA chelate, the meso isomer is more stable (log K^0 = 39.0) than the racemic isomer (log K^0 = 37.9) (*3*). The stability constants for Fe−EDDHA isomers showed that the Fe−ligand stability constant was 2.26 log units greater for the racemic complex than for the meso complex, indicating a ~200-fold difference in iron chelating ability (*2*). The different stability trends between isomers for Fe−EDDHMA with to respect Fe−EDDHA may be due to the close presence of the two methyl groups (see Figure 1A) in *rac*-Fe−EDDHMA. This steric interaction between the methyl groups does not occur in *rac*-Fe−EDDHA but may reduce the stability of *rac*-Fe−EDDHMA with respect to *meso*-Fe−EDDHMA.

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Fe(II)—EDDHA and —EDDHMA Sorption

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Adsorption or "fixation" of chelating agents in soils was recognized in early investigations of the agricultural uses of synthetic chelating agents (*4–12*). The effectiveness of Fe chelates as Fe sources and carriers in soil can be severely limited by the adsorption of Fe chelates or chelating agents in the solid phase (*13*). The factors affecting adsorption include the type of chelating agent, the metal ion, time, pH, salt concentrations, and soil texture (*12*). Wallace et al. (*5*) added various chelates including Fe(III)—EDDHA to soils and found that in 4 days chelating agent losses in a calcareous loam ranged from 7 to 30%. Losses in a moderately acid clay soil ranged from 0 to 51%. Adsorption, rather than degradation, was identified as the cause of the losses.

Despite the involvement of adsorption in virtually all studies of metal chelate reactions in soils, neither the mechanisms nor the sites of adsorption are known. This is not surprising considering the diversity of chelate species and soil surfaces that may be involved. Wallace and Lunt (*6*) and Lunt et al. (*14*) implicated the clay-size fraction of soils as the major adsorbent of chelating agents. This suggestion is undoubtedly correct because the clay-size fraction of soils contains the majority of the surface (*12*), but it does not identify which mineral or organic surfaces are important. As would be expected, the negatively charged surfaces of clay minerals were not effective at adsorbing the predominately anionic chelate species (*15, 4*), and positively charged sites on iron oxides and other colloids were suggested to be more important. Adsorption of chelating agents by peat was also observed, and losses of EDDHA from Fe—EDDHA can be relatively large at low pH (*16*).

Negatively charged chelates adsorption by surfaces with pH-dependent charge, such as oxides or peat, decreases with rising pH (*17*). Benjamin and Leckie (*18*) have called this behavior ligand-like adsorption in contrast with metal-like adsorption, which increases with pH.

Adsorption of chelates by specific iron oxides may be similar to what occurs with soil oxides (*12*). The net surface charge of iron oxides is pH dependent, changing from predominately positive at low pH to negative at high pH. The point of zero charge is usually >pH 7 and often as high as pH 9. The point of zero charge of a synthetic ferrihydrite, like the one used in this study, is around pH 8 (*19*). Adsorption of several anionic ligands, including EDTA and DTPA, by the iron oxide hematite was found to decrease slowly as pH increases from about 3 to 10 (*20*). Adsorption occurs at pH levels above as well as below the point zero charge, showing a degree of specific chemisorption in the binding of these anionic ligands in opposition to the net negative surface charge. Another indication of specific surface reactions was that the adsorption of EDTA added negative charge to the surface, thereby reducing the point zero charge from a pH of about 7 to pH 4.

The adsorption of metal chelates by soils remains poorly understood. Full understanding of these reactions will always be impeded by the complexity of soil surfaces, continuing changes in chelate speciation, and concurrent degradation of the chelating ligand. No previous work deals with differences in sorption of isomers of the same chelates. Since they differ greatly in their iron chelating capacity, it may be hypothesized that they differ also in sorption behavior. A study of sorption of the individual isomers of Fe—EDDHA and Fe—EDDHMA by well-characterized solid phases using a highly specific chromatographic method (*21*) to quantify the recoveries of chelate is presented in this paper to better elucidate the nature of chelate adsorption in soil.

Another major problem to carry out these types of studies is to find an adequate method to determine the losses of chelate. In Europe, there is no official method recognized to quantify iron chelates. Different analytical methods have been used to measure the amount of iron chelate recovered after interaction with solid phases. An isocratic HPLC ion-pair chromatographic method to identify and quantify iron chelates has been reported by Lucena et al. (*21*) and Hernández-Apaolaza et al. (*22*). Ferric chelates of EDDHA, EDDHMA, and several other ligands were well-separated by this method. Separation, quantification, and identification of the ferric complexes were obtained with good resolution and selectivity, including the separation of the meso and racemic isomers of the complexes, in 15 min per analysis. In this study, the HPLC method is used to determine the degree of adsorption of each isomer of the iron chelates Fe—EDDHA and Fe—EDDHMA on several soil materials.

MATERIALS AND METHODS

Soil Materials. Three materials were used as model compounds. A standard of calcareous soil, using the three of these compounds together, gave similar reaction with commercial chelates than a calcareous soil from Sudanell, Spain (*23*). Ferrihydrite was chosen among the soil iron sesquioxides because of its high reactivity (*24*). Ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) was prepared in the laboratory following the procedure of Sims and Bingham (*25*) by mixing an $FeCl_3 \cdot 6H_2O$ (Probus) solution with NaOH (Fe/OH = 3.0) at room temperature. The precipitate was filtered and washed first with distilled water, left to stand in contact with water over 24 h, filtered, and then washed with ethanol (80%) to attain a pH value of the wash water of approximately 6.0. The brown-red precipitate was dried at 65 °C over 48 h and pulverized. The material was identify by X-ray diffraction with a Siemens D-5000 apparatus, Cu radiation Kα (λ = 1.54184 Å), raw data measured from 10° 2Θ to 70° 2Θ, and time/step = 1.0 s, stepsize 0.02. This iron(III) oxide corresponded with a ferrihydrite phase of 6 lines, similar to those described by Drits et al. (*26*) and had a surface area value of 220 m² g⁻¹, which was determined by using the BET equation (*27*) for nitrogen (N_2) adsorption after degassing the sample for 24 h at 196 °C.

The acidic mountain *Sphagnum* peat was provided by Tolsa S.A. (Buyos, Lugo, Spain), and it is normally used as an organic amendment or substrate for cash crops in Spain. Its chemical characteristics were as follows: pH (saturated paste), 4.0; dichromate oxidizable OM (%), 85.4; total OM (%) (determined by lose of weight by ashing), 99.5; C in humic acids (%), 30.2; C in fulvic acids (%), 18.3; N_{kj} (%): 1.4%; C/N, 35.4; CEC (cmol$_c$ kg⁻¹), 150; and DTPA-extractable Fe and Mn (*28*), 295 and 8.2 mg kg⁻¹, respectively. More detailed chemical characteristics are provided by Dorado et al. (*29*).

Calcium-montmorillonite (STX-1, González County, TX) was obtained from the Clay Minerals Society Source (Clay Minerals Repository, Department of Geology, University of Missouri, Columbia, MO). This reference material has been well-characterized elsewhere (*30*), so despite its differences with typical soil smectites, it has been consider an acceptable model for soil smectites. Also, a similar material is used in the mixed substrate "enarenado" in greenhouse-grown horticultural crops in southeast Spain.

Iron Chelate Standard Solutions. For preparing the standard solution of Fe(III)—EDDHA, H$_4$EDDHA (Sigma lot 117f50221) was dissolved in sufficient NaOH (normally 1:3 molar ratio). Then an amount of Fe(NO$_3$)$_3$ that was calculated to be 5% in excess of molar amount of ligand was added, the

pH was adjusted with NaOH 1 M to 7.0, and the solution was left to stand overnight to allow excess Fe to precipitate as oxides. The solution was filtered with Whatman No. 2 filters and made up to volume with water. The final solution had an iron concentration of 100 mg L^{-1}.

As Fe(III)−EDDHMA was the reference solution and because a high-purity chelating agent was not available in the market, a commercial formulation of this chelate, Bolikel (lot 930222), was used. The Fe−EDDHMA concentration of this commercial product (4.78% of chelated Fe) was estimated from a standard Fe−EDDHA calibration curve, and the results were recalculated by using the Beer−Lambert equation corrected with the molar absorptivities coefficients of Fe−EDDHA and Fe−EDDHMA (*3, 31*). A solution of the commercial product containing 100 mg of Fe/L based on its Fe content was prepared by dissolving the formulation in deionized water. The solution was left to stand overnight, filtered through Whatman No. 2 filters, and made up to volume. The pH of the Fe(III)−EDDHMA solution was 6.7. For both solutions, light exposure was avoided during their preparation process because of the potential photodecomposition of chelates (*32*).

Sorption Isotherms and pH Variation Curves. The adsorption of chelates was determined using a batch equilibrium method similar to that of OECD (*33*). In 50-mL polyethylene bottles, 100 mg of each material was shaken with 10 mL of Fe−EDDHA and Fe−EDDHMA solutions at concentrations of 0, 1.0, 2.0, 3.0, 4.0, 5.0, 7.5, 10, 25, 50, and 100 mg of Fe/L. For Ca-montmorillonite sorption studies, solutions were prepared on 0.01 M CaCl$_2$.

Interaction conditions such as shaking mode, speed, temperature, time, and still time were done according Álvarez-Fernández et al. (*34*). So, after the bottles were shaken for 1 h at 25 °C and at 56 cycles min^{-1}, the samples were allowed to stand for 3 days in a water bath at 25 °C. Then the supernatant was filtered through 0.45-μm Millipore membranes, pH was measured, and two different aliquots were separated. In one, after the addition of 6 M HCl (10 mL of sample:1 mL of 6 M HCl), total Fe was determined by AAs, and the other was injected in the HPLC system following the Lucena et al. (*21*) chromatographic method. Three replications were done in all analytical determinations.

Isomers sorption data were fitted to the Langmuir equation

$$C_s = \frac{KC_m C_e}{1 + KC_e}$$

where C_s is the concentration of each isomer sorbed (μmol g^{-1}) after equilibration, C_e is the equilibrium concentration in solution (μmol L^{-1}), C_m (μmol g^{-1}) is the maximum chelate sorption, and K (L μmol^{-1}) is a constant related to the binding energy. C_s is calculated from the difference between initial (C_i in μmol L^{-1}) and equilibrium (C_e) solution concentrations:

$$C_s = (C_i - C_e)\frac{V}{M}$$

where V and M are the chelate solution volume (L) and material mass (g), respectively, used in the batch experiment.

C_m and K are obtained in the fitting procedure, using the solver feature of Excel, minimizing the sum of squares of the differences between calculated and experimental C_s.

The effect of pH on chelate adsorption was studied in a similar way for the pH-dependent charge materials (ferrihydrite and peat), but in this case, 100 mg of the materials was mixed with 10 mL of the Fe chelate solutions with a constant concentration of 10 mg of Fe L^{-1}, at various pH values ranging between 2 and 12.

Ion-Pair Chromatographic System. Chelate separation into its isomers and their quantification (*21, 31*) was developed by using a Waters 2690 separation module (Alliance) and a Waters 996 photodiode array detector. A Symmetry RP = 18, i.d. 150 × 3.9 mm and d_p = 5 μm column, was used. The injection volume was of 20 μL, and flow rate was 1.5 mL/min. The mobile phase contained 0.03 M tetrabutylammonium
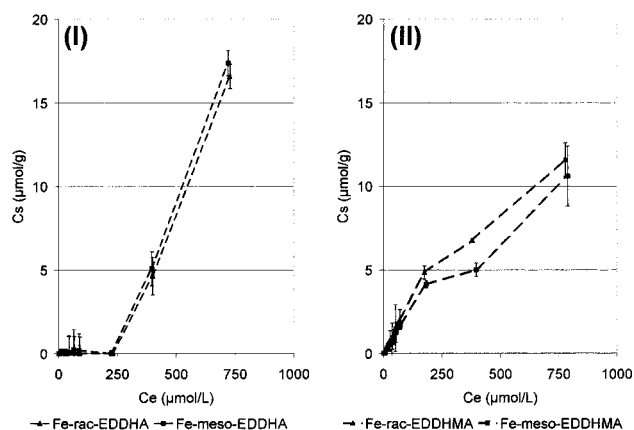
Figure 2. Sorption isotherms of Fe−EDDHA and Fe−EDDHMA chelates on Ca-montmorillonite. (I) Racemic and meso isomers of Fe−EDDHA and (II) racemic and meso isomers of Fe−EDDHMA, pH 7.23 ± 0.10.

hydroxide (40% solution in water, 1.5 M, Sigma) and 30% acetonitrile (HPLC-grade, Fisher Chemicals) at pH 6.0. Data were processed using Millenium 2010 chromatography data system (Waters). Detection limit is 0.1 μmol L^{-1} for each isomer.

RESULTS AND DISCUSSION

Sorption in the Presence of Ca−Montmorillonite. The adsorption of Fe−EDDHA chelates (Figure 2I) shows a characteristic "S" type behavior according to the Giles classification (*35*). The Fe−EDDHMA chelates (Figure 2II) described a type "L" isotherm according to the same classification. At low concentrations, the retention of the Fe−EDDHMA chelate is greater than that of the Fe−EDDHA chelate, but as well as the concentration increased, the inverse situation occurs. The behavior of both meso and racemic isomers of Fe−EDDHA chelate in contact with Ca-montmorillonite is similar (Figure 2I).

Both Fe−EDDHMA isomers also describe similar sorption isotherms (Figure 2II). This chelate shows a different behavior in comparison with Fe−EDDHA because at a low concentration of recovered Fe−EDDHMA the adsorption isotherm is almost linear. At a high concentration of chelate, the concentration of the equilibrium solution is greater for Fe−EDDHA than for Fe−EDDHMA.

It is known that an outer-sphere complex is formed between montmorillonite and Ca cation in which two layers of silicate are bound by a Ca cation solvated by six water molecules in octahedral coordination (*36*). Probably, the iron chelate forms the complex montmorillonite−Ca−Fe−chelate through the cation because the ferrated chelates are negatively charged. This hypothesis is supported by the fact that both meso and racemic isomers behave similarly since the proposed mechanism depends on the net charge more than on the internal arrangement of the molecules.

Juárez (*37*) observed a sorption pattern similar to that of Fe−EDDHA for Na$_2$−EDTA on the same soil material and proposed that, at low concentration of recovered chelate, the solvent (in that case water) is preferentially retained on the clay surface and that the surface sites may be blocked for the chelate retention, while at high concentrations of the initial solution, the water molecules became displaced by chelate. It was like a competitive mechanism between water molecules and chelate ones. The similar behavior between free EDTA

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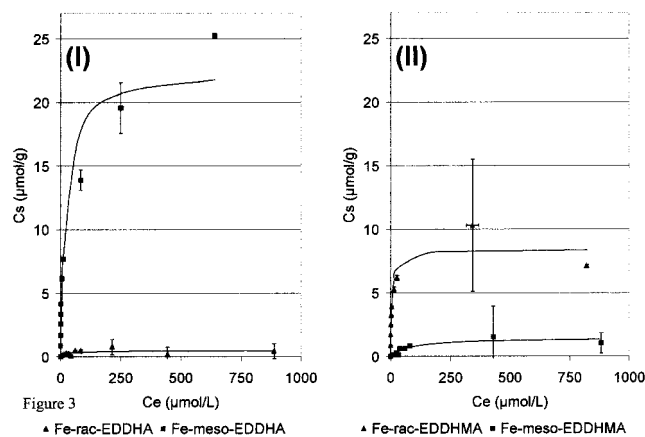
Figure 3. Sorption isotherms of Fe−EDDHA and Fe−EDDHMA chelates on ferrihydrite. (I) Racemic and meso isomers of Fe−EDDHA and (II) racemic and meso isomers of Fe−EDDHMA, pH 6.80 ± 0.48.

and Fe−EDDHA suggests that the interactions with the clay surface do not depend on the metal chelated.

Sposito (*36*) describes the presence of three different sorption sites in montmorillonite with different reactivity. Two of them could be related with exchange reactions at the exsternal and internal planes, respectively, and the third could be related to a partial hydrolysis of the montmorillonite edges. That fact could explain the shape of the sorption isotherms obtained for the Fe−EDDHMA chelate because the curve presents a change of slope possibly due to the sorption on a new surface. The presence of two different sorption sites could also explain that the data obtained do not fit the Langmuir equation, and the same fact occurs with data presented by Juárez (*37*) for the same soil material.

Sorption in the Presence of Ferrihydrite. Fe−EDDHA and Fe−EDDHMA retention by the iron oxide ferrihydrite is shown in Figure 3. Both compounds present similar behavior and describe a type L curve according to the Giles classification (*35*). A higher adsorption of Fe−EDDHA in comparison with Fe−EDDHMA was observed.

The Fe−*meso*-EDDHA isomer (Figure 3I) is highly adsorbed on this oxide, but the racemic isomer is not significantly retained by ferrihydrite. In the case of Fe−EDDHMA isomers, Figure 3II shows that the racemic isomer was more retained by the oxide but also that a small sorption of the meso isomer was observed. Despite that most of the assumptions that were made to develop the Langmuir equation are not valid for heterogeneous surfaces found in oxyhydroxides, it can be used for purely qualitative and descriptive purposes (*38*). Data obtained for the sorption on ferrihydrite fitted adequately to the Langmuir equation. Table 1 shows the sorption coefficients of the Langmuir equation. The C_m coefficient (maximum chelate sorption for the ferrihydrite) shows great differences between the retention of Fe−EDDHA and Fe−EDDHMA isomers on ferrihydrite. Fe−*rac*-EDDHA is poorly adsorbed by the iron oxide, but Fe−*rac*-EDDHMA has greater retention on ferrihydrite. With the meso isomer a similar situation occurs. Fe−*meso*-EDDHA presents higher C_m value and double K coefficient than Fe−*rac*-EDDHA. So this isomer must be more strongly retained by the oxide than the Fe−*rac*-EDDHA.

The pH of the interaction assay was 6.8. At this pH (below its point zero charge) the ferrihydrite surface is

Table 1. Sorption Coefficients of the Langmuir Equation Calculated for the Interaction between Ferrihydrite and Fe−EDDHA and Fe−EDDHMA Chelates at pH 6.80 ± 0.48[a]

|	C_m (μmol g^{-1})	K (L μmol^{-1})	r
Fe−EDDHA			
racemic	0.476	0.035	0.666
meso	22.5	0.044	0.976
Fe−EDDHMA			
racemic	8.42	0.163	0.920
meso	1.46	0.012	0.669

[a] C_m, maximum chelate sorption for the ferrihydrite; K, binding energy-related constant.
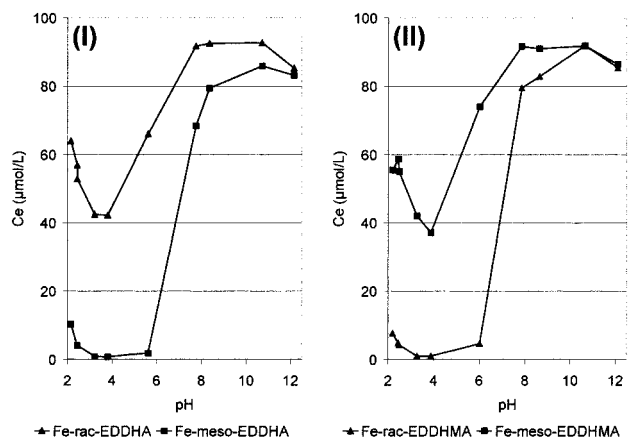
Figure 4. Variation of the sorption of Fe−EDDHA and Fe−EDDHMA chelates on ferrihydrite with respect to the pH of the solution. (I) Racemic and meso isomers of Fe−EDDHA and (II) racemic and meso isomers of Fe−EDDHMA, pH 4.45 ± 0.07.

positively charged and the iron chelates are negatively charged, so an electrostatic link between the -OH$_2$$^+$ of ferrihydrite and the molecule of chelate could be formed. In that case, the sorption of both isomers of the chelates must be almost equal as well as the sorption of both types of chelates, but this does not occur. Models of the sorption of ions by iron oxides developed in recent years suggest that the surface of oxides is composed of multiple sorption sites with different binding strengths (*39−41*). Probably, the Fe−EDDHA and Fe−EDDHMA were adsorbed in different sites of the ferrihydrite surface. Another possibility is that the chelate lose some of their links with the Fe, probably the ones with the carboxyl groups, which are less stable, and then formed an electrostatic binding with the ferrihydrite surface. The stability of the chelates is now an important fact to understand the sorption process. First of all, the Fe−EDDHMA chelates present higher stability constants than the Fe−EDDHA, so Fe−EDDHMA opens its spatial arrangement in a more difficult way than the Fe−EDDHA, and they will be less adsorbed at the surface (Figure 3). For the Fe−EDDHA isomers, the meso is more retained than the racemic, which is related to its stability constants too (log $K_{Fe-meso-EDDHA}$ = 33.28 and log $K_{Fe-rac-EDDHA}$ = 35.54; *2*). For the Fe−EDDHMA isomers, the same situation occurs (log $K_{Fe-meso-EDDHMA}$ = 39.00 and log $K_{Fe-rac-EDDHMA}$ = 37.90; *3*).

The variation of the sorption with pH for this material was also tested. Chelated Fe in the equilibrium (C_e) data (Figure 4) showed that the retention of Fe−EDDHA and Fe−EDDHMA followed a similar tendency with pH changes. At low pH, the soluble iron concentration increased due to the dissolution of the ferrihydrite.
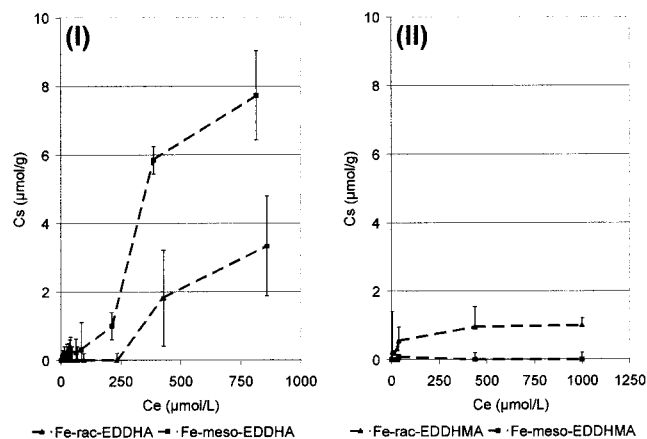
Figure 5. Sorption isotherms of Fe−EDDHA and Fe−EDDHMA chelates on peat. (I) Racemic and meso isomers of Fe−EDDHA and (II) racemic and meso isomers of Fe−EDDHMA.

Figure 6. Variation of the sorption of Fe−EDDHA and Fe−EDDHMA chelates on peat with respect to the pH of the solution. (I) Racemic and meso isomers of Fe−EDDHA and (II) racemic and meso isomers of Fe−EDDHMA.
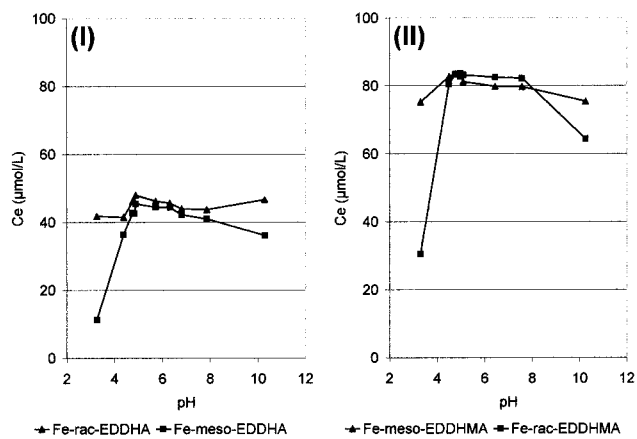
Between pH 4 and pH 8, both chelates were largely retained by the iron oxide, but over the isoelectric point that corresponded to pH 8 for a synthetic ferrihydrite (*19*), C_e increased, close to the initial levels: the sorption drastically decreased because the oxide became negatively charged. For the Fe−EDDHA chelate (Figure 4I), the meso isomer is more strongly retained by the surface along the pH range tested, but for the Fe−EDDHMA chelate (Figure 4II), the racemic isomer is more retained. In addition, the stability considerations previously discussed support the hypothesis that one or two carboxyl groups of the chelates break their link with the Fe and electrostatically interact with the oxide surface when it is positively charge.

Sorption in the Presence of Peat. Fe−EDDHA retention in peat is greater than Fe−EDDHMA retention (Figure 5). This fact was previously described by Gárate and Lucena (*42*) and Álvarez-Fernández et al. (*34*) by using AAs and colorimetric measurements. Álvarez-Fernández et al. (*34*) determined that the relation between total Fe (AAs) and chelated iron (colorimetric measurements at 480 nm) that remains in solution after interaction with a soil standard with the same peat used in this work was 1:1. That means, that the whole chelate was retained by peat surface.

According to Figure 5I, the shape of sorption isotherms for both isomers of Fe−EDDHA are included in type S (*35*). The most retained isomer of Fe−EDDHA on the acid peat surface is the meso isomer, possibly due to its lower stability constant in respect to the racemic one. The mechanism of sorption of Fe−EDDHA on peat surfaces are not known, but the higher retention of the Fe−*meso*-EDDHA could suggest an electrostatic process where Fe^{3+} can be the binding element. For Fe−EDDHMA, the sorption isotherms (Figure 5II) revealed that the adsorption is very low for racemic and meso isomers. This could be also related to the stability constants. Because these isomers are more stable than the Fe−EDDHA ones, iron is not allowed to contact peat surface, and no sorption was observed.

Sánchez-Andréu et al. (*13*) obtained sorption isotherms for several soils with different percentage of organic matter, concluding similar to our findings that sorption of the chelate was proportional to the concentration of the Fe−EDDHA solution added.

A competitive process may occur between the cations in solution and the iron for the chelating agent EDDHA.

The Fe displaced from the chelate is adsorbed by peat surface as well as an amount of the Fe−EDDHA chelate. Kreij (*43*) observed that, when Fe−EDDHA was added to peaty substrates, the Mn, Zn, and Cu contents in the water extracts increased, even without the addition of these micronutrients. The iron chelate may act as an extractant from peat, thus elevating the water-soluble levels of Mn, Zn, and Cu.

Sorption data do not fit to the Langmuir equation, possibly due to the multiple and different sorption sites present in peat that make the sorption mechanism difficult to be modeled. The variation of sorption with pH was also studied on this material, and it is shown in Figure 6. Figure 6, panels I and II, shows the behavior of Fe−EDDHA and Fe−EDDHMA isomers, respectively. The Fe−EDDHA isomers are retained all over the pH range, but the Fe−EDDHMA isomers are practically not adsorbed between pH 5 and pH 9.

At extremely low and high pH, dissolution or precipitation phenomena could be responsible for iron losses. At low pH, the chelate is not stable and Fe^{3+} is in solution, and the sorption process takes place. At high pH, iron precipitates as oxides, and then sorption is less important. At neutral pH the chelate is stable, and a competition between it and peat surface occurs.

Agronomic Implications. Fe chelates are used to solve iron chlorosis in high pH soils because they can mobilize soluble iron to the root surface. Among other factors, the rate of this transport is dependent on sorption processes. Since sorption of Fe−EDDHA and Fe−EDDHMA on iron oxides and peat is higher at low pH, it will not be a very important process in high calcareous soils, which confirm previous data (*11, 13, 14, 23, 34, 42*). However interaction in high organic substrates at acidic or neutral pH could be important as Boxma (*16*) studied for Fe−EDDHA. Also interaction with substrates with highly reactive oxides, such as allophane, could be considerable if pH it is not over the zero point of charge.

For the most reactive isomers, the relative amount of chelate retained on ferrihydrite (the most reactive material) is higher when they are applied at low concentrations (Figure 3). Then in high-frequency application of fertilizer techniques, such as in fertirrigation (*44*), it would be not recommended to apply low doses with every irrigation but to apply large doses only a few times along the crop development.

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Commercial chelates contains a large amount of soluble nonchelated iron besides the Fe–EDDHA or Fe–EDDHMA (*45*). As precipitation of this Fe as fresh iron hydroxide occurs when they react with soils or horticultural substrates (*34*), more retention of the chelated Fe is expected when less pure commercial chelates are used.

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