

The potential valorization of iron ore Jerissa and Tamra as iron fertilizers in agronomy

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Article History

Received: 19.11.2023

Accepted: 06.12.2023

Published: 19.12.2023

Abstract: Iron chlorosis is a relevant and limitant nutritional disorder in plants grown in alkaline soils. Application of synthetic iron chelates is the most solution to correct this abiotic stress. Nowadays the use of these recalcitrant chelating agents is under discussion and more sustainable ways are being researched to be used as natural raw materials-based iron fertilizers. This study deals with particle analysis of iron oxides and carbonates from Jerissa and Tamra iron mines, and their preliminary potential for agricultural valorization as iron fertilizers will be assessed. Physic and chemical characterization of both iron ores will be performed by using FTIR, BET, SEM, EDX, XR and AAS analytical techniques. Batch experiments were arranged by interacting diluted solutions of ultrapure water, chelating agents (EDDS, HBED, IDHA), low molecular weight organic acids – LMWOA (citrate) and Humic substances (HS) with both tested iron ores to determine those soluble and extractable iron fractions. Batch experiments showed that Citrate, EDDS, IDHA, HS and HBED diluted solutions were able to extract large amounts of iron from both tested iron ores. High extractability rate of iron ore by Citrate and HBED confirm the potential valorization of those iron ore as mineral fertilizers.

Keywords: iron ore, fertilizers, iron chelate, complex, Tunisia, valorization.

1. INTRODUCTION

Iron deposits in the Nefza district were first exploited at the end of the 19th Century. Berthon (1922), who gave a brief and exploitation-oriented description of the mine, together with lithological series descriptions and geochemical data, described the Tamra mine. In 1950, the estimated tonnage of the Tamra mine was 1.6 Mt at an average grade of 50 % Fe (Gottis, 1952). The Tamra iron ore results from a combination of pedogenetic pre-concentration processes, linked to interaction with meteoric fluids, and hydrothermal iron (Fe) enrichment (Decrée et al., 2008a). The Jerissa mine located in north-central Tunisia. The record of a century of mining at the Jerissa mine is characterized by a cumulative production of over 40 Mt of iron ore with an average grade of 54% iron metal. Currently 100,000 t / year of hematite and 70,000 t / y of siderite. Most of Tunisia's iron ore production, about 220,000 tons, is destined for local industries moreover, small quantities of natural siderite (15 000 t) are exported annually to European countries for the cattle feed and industries (Mahjoubi, 1978; Mahjoubi et Samama ,1983).

Then, the application of iron ore in agriculture is another new alternative as it can ensure a product with fertilizing value and fit for use. The valorization of iron ore in Tunisia (iron carbonate, goethite and hematite), could be an important and profitable practice in the field of agriculture (Grioui et al.,2021). In terms of economic impact, the losses derived from the deficiency of iron in

plants because of the decreased growth and production (Fageria et al., 2002).

In agronomy, Fe is an essential micronutrient for its role in the formation of chlorophyll and in various enzymatic processes (Marschner, 1995). A low bioavailability of Fe in soil may lead to Fe chlorosis in crops (Lindsay et Schwab ,1982) . Fe chlorosis is a major nutritional disorder affecting plant development and reducing the yield and quality of many sensitive crops growing in calcareous soils (Álvarez-Fernández et al., 2005; Briat et al., 2015). Iron deficiency is one of most relevant abiotic stress affecting the fruit tree in the Mediterranean region (Bertaminiand Nedunchezian, 2005). In the Mediterranean basin, where 20-50% of fruit crops are affected by decrease in the uptake and transport of iron (Jaeger et al.,2000).

This condition requires the treatment or prevention by iron based chelates or complexes (HBED/Fe, EDDS/Fe, IDHA/Fe...) (lucena , 2006). In addition, some environmentally friendly ligands have been used to correct this problem as organics acids, humic acids, gluconic and heptagluconic acids (Villen et al, 2007).

N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED) is a strong Fe³⁺ chelating agent applied in agronomic (Lucena,2003 ; Nawrockia et al.,2009) . In 2007, Fe HBED was introduced to solve iron deficiency in plant cultivation. The effectiveness of those agents chelating to correct Fe chlorosis has

been confirmed in several plant experiments. Its structure is similar to that of o, oEDDHA (Brittenham, 1992).

Some environmentally friendly ligands have been used to solve this problem as leonardite, fulvic acids lignosulfonates, gluconic and heptagluconic acids, amino acids organic acids and flavonoids (Bergeron et al., 2002; Hernandez-Apaolazer et al., 2006; Villen et al., 2007). Although iron complexes fertilizers are cheaper, more ecofriendly and biodegradable than iron synthetic chelates they also have less effective and less stability, in correcting iron deficiency (BOE, 2005; BOE, 2007; Cesco et al., 2000; Nicolici et al., 2003; Chen et al., 1982).

Leonardite is mainly humic acid (HS) with a high-condensed structure where iron is present as ferrihydrite and Fe^{3+} poly-nuclear compounds stabilized by organic matter (Lucena et al., 2010). The good effects of humic substances may be ascribed to a general improvement of soil fertility, leading to a higher nutrient availability for plants, others seem to positively influence metabolic and signaling pathways involved in plant development (Cieschi et al., 2017; Sherman, 2002). According to the biological assay, Fe^{3+} /leonardite confirmed to be effective as a chlorosis corrector applied to iron-deficient cucumber in nutrient solution (Nardi et al., 2009).

Ethylene diamine disuccinic acid ([S,S]-EDDS) is based in natural amino acid group (L-aspartic acid) which can be fast degraded by bacteria, thus conferring it a high biodegradability (González et al., 2007; Rodríguez-Lucena et al., 2010a). [S,S]-EDDS may be an environmentally sustainable alternative to traditional synthetic chelates for curing Fe chlorosis in calcareous soil. The Fe -L stability constant of [S,S]-EDDS is $\log K^\circ = 23.7$ (Orama et al., 2002). Many works have studied the properties of the [S,S]-EDDS/ Fe chelate. Albano, 2012; Albano and Merhaut, 2012; Nowack et al., 2008 have confirmed their efficacy when applied to hydroponics. IDHA [N-(1,2-dicarboxyethyl)-D,L-aspartic acid] have been proposed as environmentally friendly and biodegradable agent to be used in fertilization with micronutrients (Lucena et al., 2008; Rodríguez-Lucena et al., 2010b). This structural difference can represent an advantage, providing Fe to plants faster than those containing six bonds (García-Marco et al. 2006, Escudero et al. 2012). Villén, García-Arsuaga and Lucena (2007). Villén et al. (2007) proved that IDHA/ Fe^{3+} is quite

efficient in providing Fe to cucumber and soybean plants grown in hydroponics at pH 7.5 in controlled conditions and related this behavior to the presence of five bonds between the Fe and the chelating agent. Low Molecular Weight Organic Acids (LMWOA) such as (oxalic, malic and citric acid) have been hypothesized by many authors to be involved in the mobilization of nutrients within the rhizosphere (Gardner et al., 1983; Hoffland et al., 1989; Hoffland, 1992; Marschner, 1995; Farrar and Jones, 2000). As these organic acids efficiently solubilized/mobilize many metal cations (Gerke, 1992, 1993, 1994; Gerke et al., 1994; Jones and Darrah., 1994).

Studies conducted by Silva et al. (2009) with Fe citrate complexes, demonstrated that at pH 9, a mononuclear Fe complex is predominant with a low Fe^{3+} /citrate molar ratio, whereas a high Fe^{3+} /citrate molar ratio at neutral pH lead to the formation of oligomeric complexes.

Complexing agents such as sodium gluconate or sodium glucoheptonate have a low environmental impact due to their high biodegradability rate (Maxwell, 2004). They can complex metals through their carboxylic and hydroxylic functional groups by different binding modes depending on the metal it self and the reaction conditions.

The aim of this work is to get a preliminary evaluation of both iron ores from Jerissa and Tamra mines to be used as iron fertilizers. The iron ores evaluation will be carried out by determining the physical and chemical characteristics and by measuring the iron solubility/extractability rate by designing batch experiments in which parameters such as extractable agents and pH values will be tested to know the solubility and extractability iron rate.

2. Materials and Methods

2.1. Study materials

Iron ore Jerissa was got from Jerissa iron mine located in the northern Centro of Tunisia of Aptian age (Figure 1a). Iron ore Tamra was got from Tamra mine that is located in northern Tunisia about 120 km NW of the city of Tunis and about ten km north of Nefza village. The Mio-Pliocene formation of Tamra consists of about 50 meters of ferruginous sediments (Figure 1b).



Figure 1. Picture of the two-iron ore Jerissa (a) and Tamra (b) located in the north of Tunisia.

2.1. Characterization of Tamra and Jerissa iron ores

In this part, our purpose is to try to describe the fundamental characteristics of the petrography, mineralogy and geochemistry of iron mine mineralization Tamra and Jerissa. The geochemical, mineralogical and petrographic studies that we will present below were carried out at the Faculty of Science Autonomous Madrid on three iron ore samples taken from the two mines studied. Several methods were used for the physico-chemical characterization of the three samples of iron ore.

2.1.1. Physical Characterization

The physical analyzes used to characterize iron ores are XRD, FTIR, SEM and BET:

The X-ray diffraction (XRD) characterization method makes it possible to highlight information on the crystalline structure of materials (for example their texture and degree of crystallinity). X-ray diffraction analyzes were performed on a Philips X'Pert diffractometer and were collected at CuK α on Rigaku D-MAX 2500 diffractometer in Theta/2Theta geometry. The powders were dispersed on aluminum sample holders.

These analyzes were supplemented by a mineralogical study based on Fourier transform infrared (FTIR) analysis. To confirm the results obtained we carried out the analysis of FTIR. Fourier transform infrared spectroscopy provides information on the nature of chemical bonds and can be used for the identification of compounds. Indeed, this technique, sensitive to the vibrations of bonds exhibiting a dipole moment, produces spectra comprising absorption bands whose position is characteristic of the bonds involved because they depend on the mass of the atoms and the strength of the bond. FTIR analysis was performed on various iron ore samples to show the contained elements and the manner in which they are chemically bound. FTIR spectra were recorded using KBr pellet method and operated with Bruker IFS66vd spectrometer (Germany) apparatus in the spectral range of 4000-500 cm⁻¹ with a resolution of 4 cm⁻¹ in the transmittance mode.

Scanning Electron Microscopy (SEM) is a technique for observing surface topography. It provides information on the structure and texture of a sample but also on the size and shape of elementary grains or agglomerates depending on the magnification chosen. The microscope is a (SEM, LEO 1455 VP, acceleration voltage 20 kV) at a working distance of 15 mm equipped with an X-ray dispersive energy spectrometer (EDS, Inca X - sight, Oxford Instrument). The analyzed samples (powders) were deposited on aluminum supports.

The Brunauer–Emmett–Teller (BET) technique was universally adopted for measuring the surface area and internal porosity of the materials by adsorption of inert gas (liquid nitrogen) on the surface

of the particles and by measuring the amount of adsorbate inert gas corresponding to a monomolecular layer on the surface. It was carried out on a quanta chrome/AUTOSORB-iQMP apparatus to determine the surface area from the nitrogen isotherm (adsorption and desorption) at -196.15 °C (77 K). Barrett-Joyner-Halenda (BJH) method is most commonly used to determine the pore size distribution of the particles.

2.1.2. Chemical characterization

Geochemical analyzes were performed by ICP-MS for minor elements (ppm) and by atomic absorption spectroscopy for major elements (%).

The content of iron was measured by atomic absorption spectroscopy (AAS, Perkin-Elmer AAnalyst 800; Shelton, CTm USA). The micronutrient concentrations in iron ore were analyzed by inductively coupled plasma mass spectrometry (ICP MS; NexION 300XX, PerkinElmer) after nitric acid digestion. Then the measurement of pH, EC and CaCO₃ were realized.

The pH and the electrical conductivity (EC) were measured in iron ore/water mixture at a ratio of 1/2.5 (w/v). The iron ore pH was measured using a WTW pH meter on iron ore/water suspension at a ratio of 1/2.5 (w/v). The measurement of the EC was carried out using an LF91 WTW electrode with an iron ore/water ratio 1/5 (Rayment and Higginson, 1992). The content of carbonates to be analyzed in the iron ore samples was determined by the Bernard Calcimeter (Afnor, 1999).

2.2. Batch experiments

In order to determine the soluble and extractable fractions from iron ore (Tamra and Jerissa) with the different agents chelating, two experiments were handled. The first experiment consisted to evaluate the solubility of iron and the extractable fraction of iron ore Jerissa (Siderite (S), Hematite and Goethite (HG)) and iron ore Tamra (Hematite/Goethite/Limonite: (T)) at pH 7.5 with 10 agents chelating/complexing (HBED, HS, EDDS, IDHA, gluconate, hyptagluconate, oxalate, citrate and malate). The second experiment released for deepen the study of extractable fraction from iron ore with the most complexing and chelating agents obtain in the first experiment. In this experiment, three samples of natural iron ore (S, HG, and T) and four agents were selected (IDHA, Citrate, HBED and HS); 12 solutions were prepared according to pH from 4 to 10 with 3 replicate and 25 ml for each pH (see Table 1). The following solutions were prepared: IDHA /Fe (S), IDHA /Fe (HG), IDHA /Fe (T), HBED/Fe (S), HBED/Fe (HG), HBED/Fe (T) , HS/Fe(S), HS/Fe (HG), HS/Fe(T), Citrate/Fe(S) ,Citrate/Fe(HG) and Citrate/Fe(T) . Then the same experiment was done with water at several pH for to know the soluble fraction of iron ore.

Table 1: The description of composition of different iron solutions prepared in the second experiment at several pH (4 to10).

Solutions	Agent chelate/complexing	Iron	Origin	Molarity	Volume
IDHA/Fe (S)	IDHA	Siderite	Jerissa mine	0.001M	25ml
IDHA/Fe (HG)		Hematite / Goethite	Jerissa mine		
IDHA/Fe (T)		Hematite/Goethite/Limonite	Tamra mine		
Citrate /Fe (S)	Citrate	Siderite	Jerissa mine	0.001M	25ml
Citrate/Fe (HG)		Hematite / Goethite	Jerissa mine		
Citrate /Fe (T)		Hematite/Goethite/Limonite	Tamra mine		
HBED/Fe (S)	HBED	Siderite	Jerissa mine	0.001M	25ml
HBED/Fe (HG)		Hematite / Goethite	Jerissa mine		
HBED/Fe (T)		Hematite/Goethite/Limonite	Tamra mine		
HS/Fe (S)	Leonardite	Siderite	Jerissa mine	0.001M	25ml
HS/Fe (HG)		Hematite / Goethite	Jerissa mine		
HS/Fe (T)		Hematite/Goethite/Limonite	Tamra mine		

- Experiment 1

The general principle of this experiment is to mix an amount of iron ores ($0.0500 \pm 0.0001\text{g}$) with the agent chelating (0.001M) in 25 ml flask. Then, added 2.5 mL of HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] universal biological buffer for adjusted the pH to 7.5, either with HCl or NaOH solutions as it was needed. After the interaction of solutions for 24 hours in an end over shaker, the solutions were centrifuged (10000/10min) and filtered (45µmm). Iron concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS Perkin-Elmer AAnalyst™ 800). The standard chelating agents used in these experiments were HBED, EDDS, and IDHA and complexing agent (gluconate, hyptagluconate, oxalate, citrate and malate) then the use of water for determine the soluble fraction of the three iron ores sample. The HBED was kindly provided by ADOB PPC, Poznan, Poland (93.72%). The HS consist of a leonardite potassium humate provided by Humin Tech, Grevenbroich, Germany. Sodium Gluconate (Sigma Aldrich, >99%) , sodium Hyptagluconate and complexing DABEER (99%, Barcelona, Spain) ,oxalate (Sigma Aldrich, %) , citrate (Sigma Aldrich , %) , malate (Sigma Aldrich , %) , Na3EDDS (Fluka, 35%) and Na4IDHA (Adob PPC, 78.1%) were used .

- Experiment 2

Iron ores solubilization rate along pH values was assessed with four chelating/complexing agents at 0.001M. For the Fe/L solutions preparation, depend to chelating agent, some ligands were dissolved in ultrapure water (0.001 M and the author agents dissolved in NaOH diluted solution. An amount of $0.0050 \pm 0.0001\text{g}$ of Hematite/Goethite, Siderite or

Hematite/goethite/limonite was placed into a 25 ml flask then slowly added 25 ml from the agent solution. The pH was maintained from 4.0 to 10.0 by using either HCl or NaOH diluted solutions as convenience. Three replicates for each pH. Solutions were left for 24 h in shaker. Solutions were centrifuged (10000/10min), filtered through a 0.45 µm cellulose membrane and chelated iron fraction was measured by Perkin Elmer Aanalyst 800 flame absorption atomic spectrometer (FAAS). Table 1 is presented the different solutions prepared in this experiment.

3. Results

3.1. Characterization of the iron ore

Those different physicochemical and mineralogical techniques XRD, FTIR, SEM, EDX, BET, AAS and ICP make it possible to identify the minerals, to specify the rate of crystallization, to detail the morphology and the size of the grains and to compare the two iron ore (Jerissa and Tamra) between them.

3.1.1. Physical characterization

The mineralogical association of the two samples of iron ore Jerissa consists of Hematite-Goethite-Siderite-Quartz-Calcite and clay minerals (Figure 2). The mineralization of the deposits of Jerissa is originally carbonated; they originated from the replacement of pre-existing limestones (Mahjoubi, 1978 and 1983; Aissaoui, 1986 and 1990). The mineralogical characterization of the iron ore of Tamra reveals that these iron contained 39% of hematite-goethite and limonite associated with halloysite - kaolinite in the form of granules (Figure 2). The gangue minerals composed by quartz cristobalite-feldspars-micas-clay minerals.

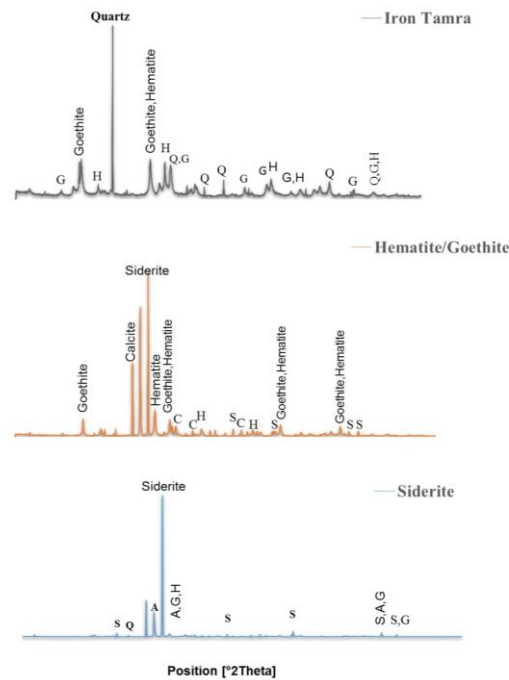


Figure 2. X-ray diffractogram of ferriferous mineralization of jerissa and Tamra. The blue curve represents the result of the Sample of iron carbonate (siderite) composed by S:Siderite;G:goethite;H:hematite; Q:Quartz;C:Calcite;A:Ankerite . The orange curve represents the result of the X-ray diffraction of sample of Hematite-Goethite compose by S: Siderite; G: goethite; H: hematite; Q: Quartz; C: Calcite; A: Ankerite. The black curve corresponds to the sample of iron ore Tamra that composed by G: goethite; H: hematite; Q: Quartz.

The FTIR spectra of siderite is showed in Figure 3. Broad bands at 3407 cm^{-1} due to the vibration of hydroxyl groups, at 1805 and 1623 cm^{-1} assigned to carboxylate anion were observed. In addition, bands at 2923 - 2856 and 2513 cm^{-1} were associated with C-H stretching vibration (Tonković, 1983) and the vibrations of Fe-O were presented in the region 1000 - 600 cm^{-1} .

The FT-IR spectra of Hematite/Goethite sample (Figure 3) presents a broad band at 3409 cm^{-1} that, according to Stevenson 1994, can be attributed to O-H stretching of carboxylic groups. The band at 2925 cm^{-1} can be assigned to aliphatic C-H stretching vibrations. Band at 1621 cm^{-1} can be due to aromatic C=C, strongly H bonded to C=O of conjugated ketones. Furthermore, according to Colombo et al., the absorption bands at 3450 - 3300 cm^{-1} correspond to O-H stretching of Fe-OH while the bands observed at 1426 , 1031 and 556 cm^{-1} can be assigned to Fe-O bonds for samples of Hematite or Goethite

The FTIR spectra of iron ore Tamra (Figure 3) presents a broad band at 3416 cm^{-1} that can be attributed to O-H stretching of carboxylic groups and Fe-OH. The band 1633 cm^{-1} correspond to C-C. Band 536 cm^{-1} can be assigned to Al-O-Si (Halloysite) and the Band at 504 cm^{-1} can be due to O-Si-O. The vibrations of Fe-O were presented in the region 400 - 300 cm^{-1}

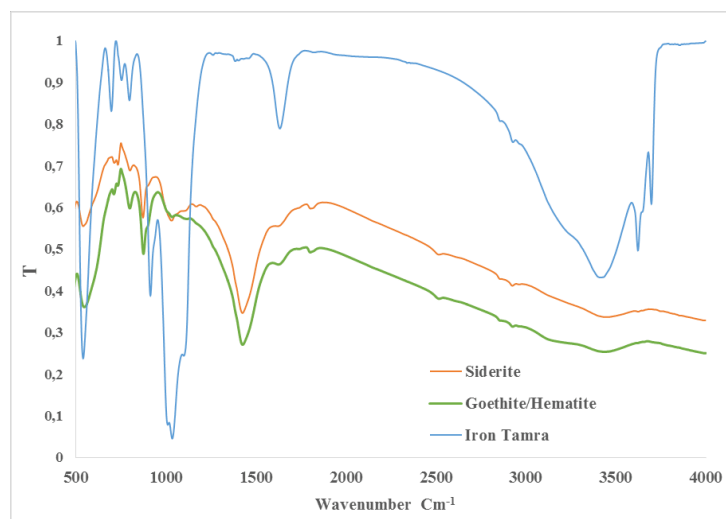


Figure 3. Infrared spectra between 500 and 4000 cm^{-1} , in orange the Siderite sample composed of siderite, calcite, hematite and goethite; in blue the Tamra iron sample composed of quartz, hematite, goethite and clay and in green the Hematite / Goethite sample composed of calcite and hematite –Goethite.

Macroscopic and microscopic examination of the first sample (Siderite) from lodge 4 shows: Siderite is the most abundant and is the protore of the mineralization of iron oxide, Hematite/Goethite. Siderite showed large and squat rhombohedra, often millimetric in size. Its color varies from beige to brown and its brilliance and vitreous (Figure 4). With SEM and EDX analysis, the second sample of iron from lodge 5 were composed by Fe, Mn, Ca, Al, Si and Mg (See Figure 5). The panoramic view of SEM of iron ore Tamra shows the following elements: Mn-Fe and Al-Si-O and the picture of 20µm shows the presence of some heavy metals as Pb, Sr (Figure 6).

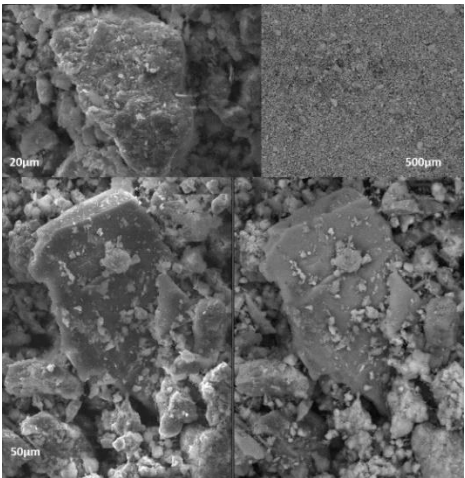


Figure 4. SEM images observed in the Siderite sample (500µm, 50µm and 20µm).

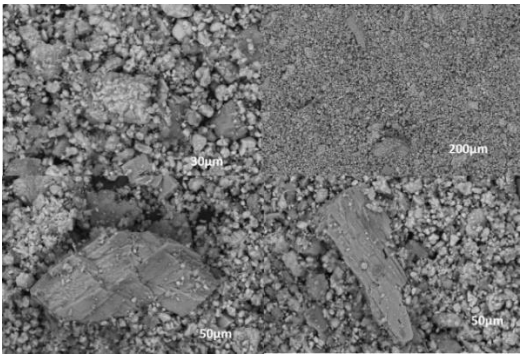


Figure 5. SEM images observed in the Hematite/Goethite sample (200µm, 50µm and 30µm).

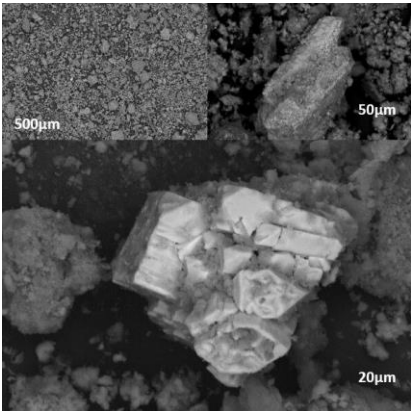


Figure 6. SEM images observed in iron ore Tamra sample (500µm, 50µm and 20µm).

The results of surface area are showed in Table 2 iron ore of Jerissa is characterized by a higher crystallized rate ($4.48 \pm 0.17 \text{ m}^2/\text{g}$ for siderite and $9.36 \pm 0.17 \text{ m}^2/\text{g}$ for Goethite/Hematite). Besides, the iron ore of Tamra shows a weak crystallization (granules and friable structure, area surface BET = $54.9895 \pm 0.1065 \text{ m}^2/\text{g}$).

Table 2: Surface area BET (m^2/g) of the different iron ore samples (Siderite, Hematite/Goethite and iron ore Tamra).

Samples	Iron ore Jerissa		Iron ore Tamra
	Siderite	Hematite /Goethite	Hematite /Goethite /limonite
Surface BET area	$4.4766 \pm 0.1670 \text{ m}^2/\text{g}$	$9.3560 \pm 0.1671 \text{ m}^2/\text{g}$	$54.9895.1065 \text{ m}^2/\text{g}$

3.1.2. Chemical characterization

Chemical content presented in Table 3 reveal that the first sample (Siderite) contains siderite 53.0% with calcite 9.02%, 2.37% MgO and 2.51% SiO₂. The second sample (Hematite-goethite) shows 65.23% Fe₂O₃, calcite (9%) and 3.31% SiO₂ as major elements. The metallic trace elements at the level of both samples remain as low compared to the pollution index and with the AFNOR NFU44_041 standards. The chemical analysis by AAS and ICP indicate that iron ore Tamra constitute by 54.83% of FeO₃, 19.46 SiO₂ %, 9.74% Al₂O₃ , 0.94% Mn, 0.52% CaO and 1516 ppm of Zn.

Table 3: The geochemical composition (percentage) of the three samples of iron ore

	Iron ore Jerissa		Iron ore Tamra
	Hematite/Goethite	Siderite	Iron Tamra
% Fe ₂ O ₃	65.23	53.06	54.83
% SiO ₂	3.31	2.51	19.46
% Al ₂ O ₃	0.04	0.09	9.74
% MgO	1.71	2.37	0.24
% CaO	9.00	9.02	0.52
% K ₂ O	0.15	0.30	0.52
% Na ₂ O	0.06	0.08	0.36

The sample of siderite characterized by pH = 8.09, CE = 451 μ S/cm and CaCO₃ = 20.3%. Hematite/goethite characterized by pH= 8.23, CE= 182 μ S/cm and CaCO₃= 29.8%. Then, the main chemical properties of ore iron are pH: 5.01; CE: 136 μ S / Cm; Ca CO₃: 4.27%.

If we compare into the two-iron ore (Jerissa and Tamra), there are same mineralogical and chemical propriety with same differences. The Jerissa iron deposits (Siderite, goethite and hematite), where a very large percentage of iron and carbonate (calcite, ankerite) has been registered which makes the pH of iron ore jerissa very high (greater than 8). However, no calcite was found for the iron ore Tamra (low pH = 5.01) but high amount of clays (Kaolinite, smectite, chlorite, illite) with multiple morphology were found Tamra iron ore also contains silica, quartz, alumina, and halloysite in the form of tubes. In both mines, there was a significant amount of manganese. Moreover, the iron ore of Jerissa shows a higher crystallized surface area but the iron ore of Tamra shows a weak crystallization (54.9895 $\pm$ 0.1065m²/g).

3.2. Batch experiments

3.2.1. Reactivity and solubility of iron ore with the agents chelating/complexing

- Experiment 1

Iron ore Jerissa:

At pH 7.5, the siderite was extractable only with five complexing agents (EDDS, IDHA, Gluconate, citrate and HBED) with different content. The rest of agents (Oxalate, Malate, HS, hyptagluconate and Water) were showed zero reactivity with siderite at this pH. Those best results were obtained for the EDDS then IDHA synthetics chelate agents. Similar rate was got for Citrate with the same quantity of extractable iron. In addition, gluconate could complexing siderite with a small content and the HBED was solubilize only a low percent of natural iron at pH 7.5. (Figure 7)

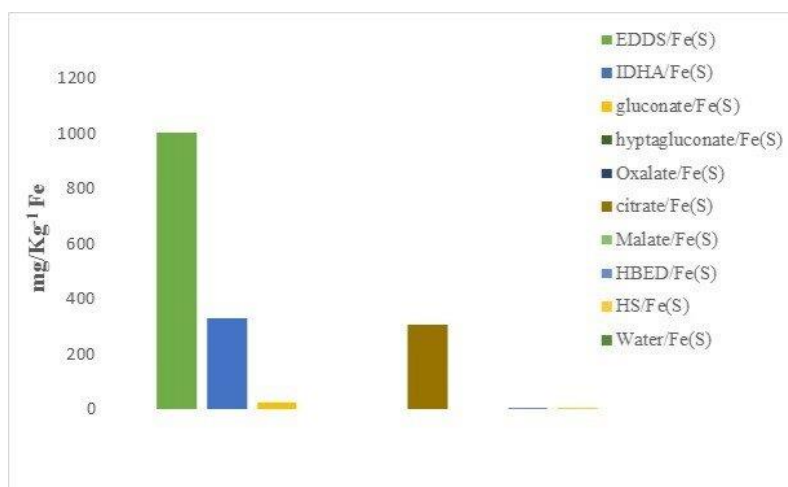


Figure 7: Extractable and soluble iron (mg/Kg⁻¹) remained in solution after 24h of interaction of iron ore Jerissa (Siderite) with different agents chelating/complexing (EDDS, IDHA, gluconate, Hyptagluconate, Oxalate, Citrate, Malate, HBED, HS and water) at pH 7.5.

The interaction of Hematite/goethite and complexing /chelating ligands was showed well results than the interaction recorded with siderite. The HG was extractable with EDDS, Citrate, and IDHA, gluconate, HBED and hyptagluconate (see Figure 8). The best results were getting by EDDS in the first order then Citrate and IDHA. The solutions prepared by complexing agents gluconate and hyptagluconate were recorded a weak quantity of extractable iron from HG. Oxalate, Malate, HS and Water were showed no solubilization with HG at pH 7.5.

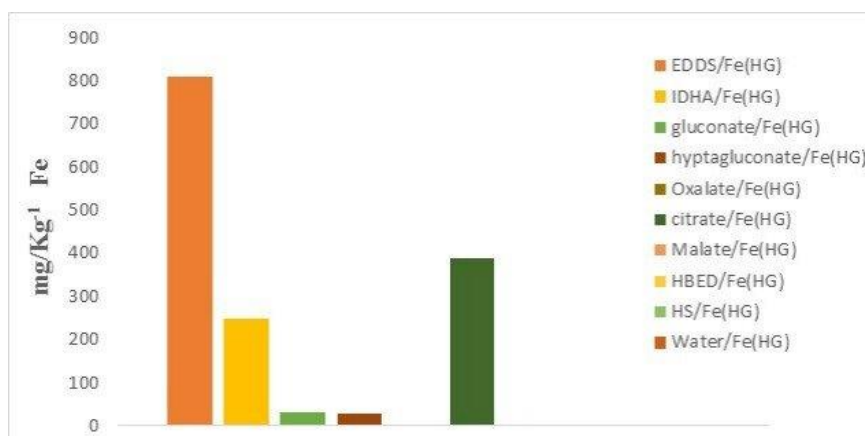


Figure 8: Extractable and soluble iron (mg/Kg^{-1}) recovered in solution after 24h of interaction of iron ore Jerissa (Hematite/Goethite: second sample) with different agents chelating/complexing (EDDS, IDHA, gluconate, Hyptagluconate, Oxalate, Citrate, Malate, HBED, HS and water) at pH 7.5.

Iron ore Tamra:

For the iron ore Tamra, the results of extractable iron were unlike to the results were recorded by the two samples of iron ore Jerissa. Iron ore Tamra was extractable with the all complexing/chelating ligands without exception but with different quantity of iron chelate (Figure 9). The best agent reacted with Tamra iron was the organic acid citrate with a higher percentage. Then, the chelating ligand HBED was in the second order. In the third order, we find the agent Humic Substance. IDHA can make natural iron extractable in solution at pH 7.5 with an average amount. The last when we compared with the amount of extractable iron recorded in EDDS/Fe (T) solution, was considered as a good complexing agent.

Gluconate/Fe(T), hepta gluconate/Fe(T), oxalate/Fe(T) and malate/Fe(T) solutions were showed a low amounts of extractable iron (less than 100mg/Kg Fe) when compared with the other solution prepared as Citrate/Fe(T). The amorphous crystal system and the weak surface area of iron ore Tamra were the principal factors for the high solubility/extractability recorded in the different iron solutions prepared at pH 7.5.

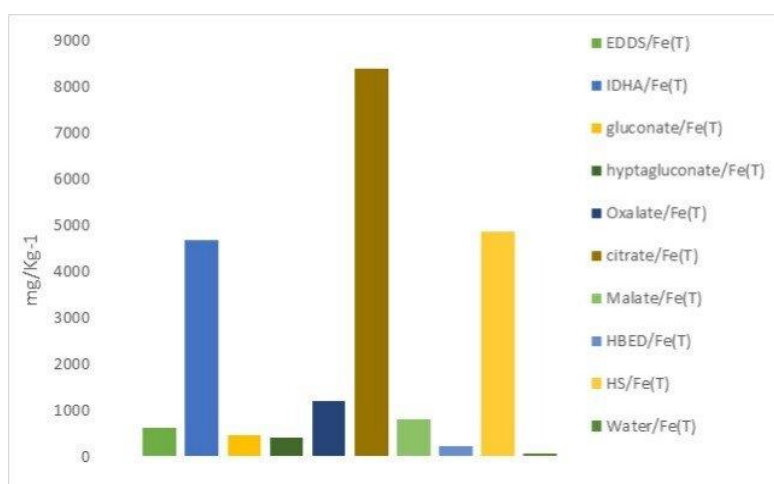


Figure 9: Extractable and soluble iron (mg/Kg^{-1}) remained in solution after 24h of interaction of iron ore Tamra (Hematite/Goethite/Limonite) with different agents chelating/complexing (EDDS, IDHA, gluconate, Hyptagluconate, Oxalate, Citrate, Malate, HBED, HS and water) at pH 7.5.

- Experiment 2

The second experiment was consisted to test the extractability of iron ore Jerissa and Tamra at pH range from 4 to 10 with several complexing/chelating agents. After the analysis of iron solutions by AAS, different results were obtained.

First, the solutions prepared with siderite and the ligands were reveals that iron extractable at pH 4 and 5. A low content of extractable iron remains in solution until pH 8 and 9 from HS/Fe (S). IDHA/Fe (S) and citrate/Fe (S) showed a low iron extractable at all pH (Figure 10).

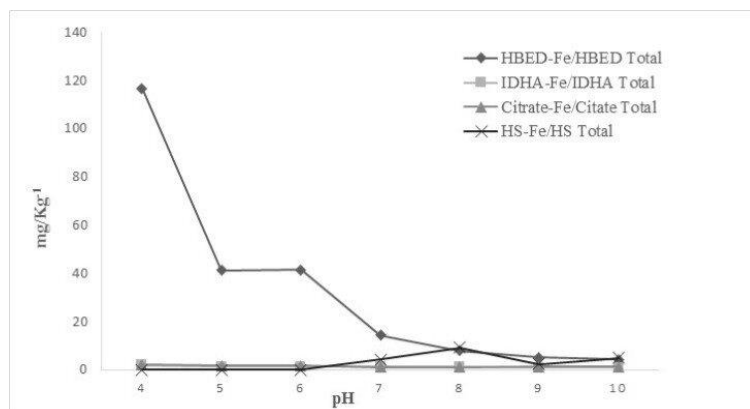


Figure 10: The amount of extractable iron from each iron solution (HBED/Fe (S), IDHA/Fe (S), Citrate /Fe (S) and HS/Fe(S)) prepared with natural iron (Siderite) and 4 agents (HBED, IDHA, Citrate and HS) between pH4 and 10 with 3 replicates for each pH.

This experience devoted to testing hematite / goethite as natural iron with different chelating /complexing agents to understand their interaction and solubility in aqueous solution. Despite that Hematite / Goethite from Jerissa was characterized by a basic pH and rich in calcite. The latter during their interaction with agents from pH 4 to 10 shows that it was extractable only at acid pH 4 and 5 with HBED and at pH 8,9 with HS. But with citrate and IDHA ligands reveals a low extractability (Figure 11)

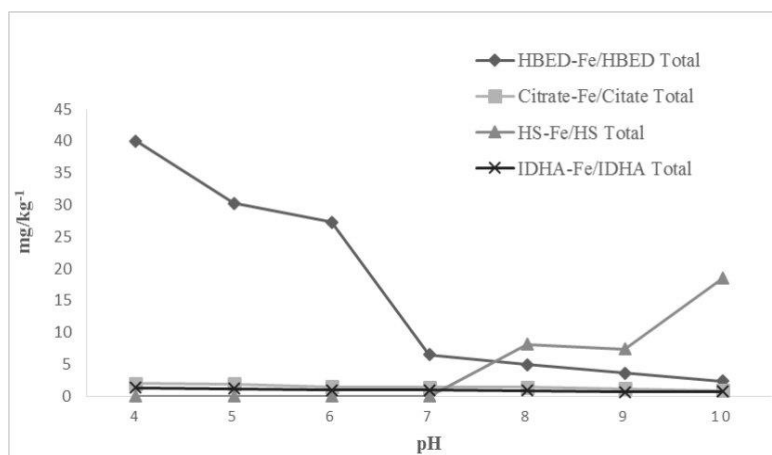


Figure 11: The extractable iron from each iron solution (HBED/Fe (HG), IDHA/Fe (HG), Citrate /Fe (HG) and HS/Fe (HG)) prepared with natural iron (Hematite/Goethite) and 4 agents chelating/complexing (HBED, IDHA, Citrate and HS) between pH 4 and 10 (3 replicate in one pH for each solution).

After 24H of interaction of Tamra iron with agents at pH range from 4 to 10 (0.001M), the analyzes of the solutions prepared by FAAS shows that the Tamra iron has been very extractable at pH above 7, that is to say at pH 7,8,9 and 10. It was very low extractable at acid pH (4 and 5) with all ligands. Then the percentage of extractability differs from one agent to another. The most effective extracting agent was citrate (LMWOA) and IDHA (degradable chelating agent). Treatments with citrate/Fe(T), IDHA/Fe(T), HS/Fe(T), HBED/Fe(T) maintain more high Fe extractable in solution at highest pH.(Figure 12)

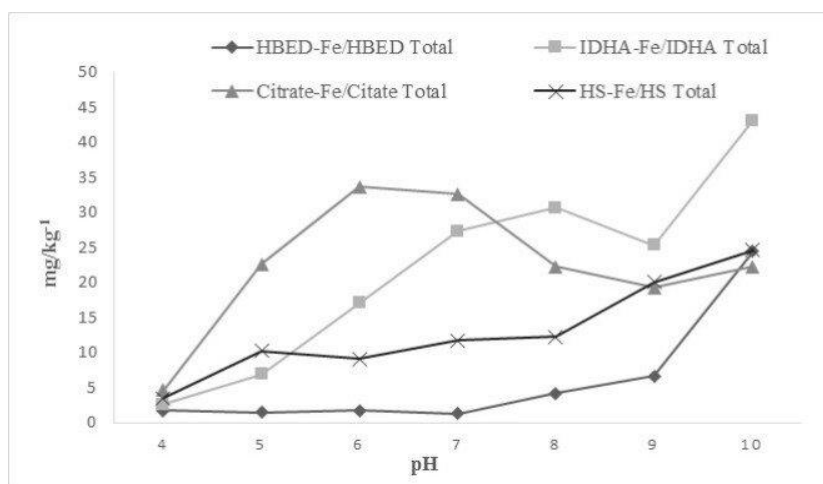


Figure 12 : The amount of extractable iron from each iron solution (HBED/Fe(T), IDHA/Fe(T),Citrate /Fe(T) and HS/Fe(T)) prepared with natural iron (Siderite) and 4 agents (HBED, IDHA,Citrate and HS) between pH 4 and 10 with 3 replicate for each pH.

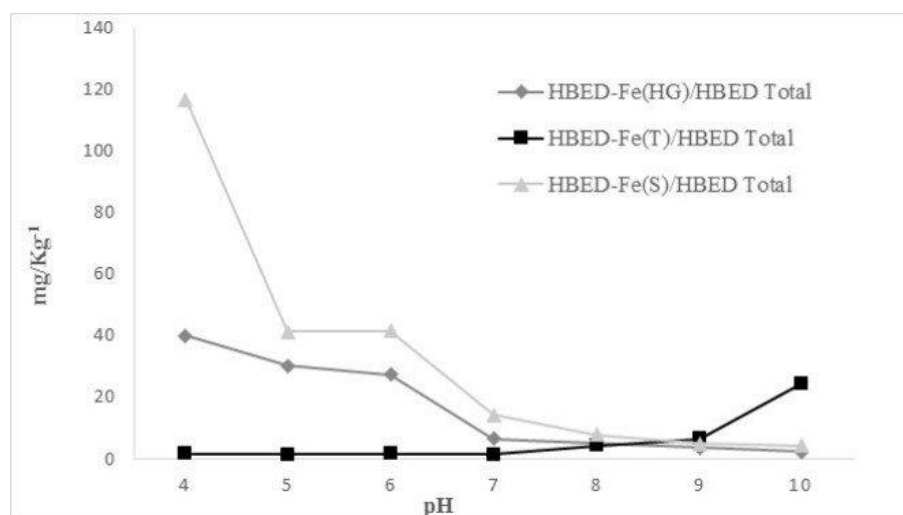


Figure 13: Comparison between the content of soluble iron in different iron solution (0.001M) prepared with HBED agent chelate and siderite (S), Hematite/Goethite (HG) and iron Tamra (T) at different pH from 4 to 10.

The percent of soluble iron that remains in Water/Fe solution after interaction at pH range 4-10 is shown in Figure 14. The results obtained in experimental assay shown that the Jerissa iron ore is not soluble in water at all pH range whatever with S or HG. Regarding Tamra iron, the figure 14 indicate that Tamra iron ore was not mobile at acid pH (4, 5 and 6) but at neutral pH and at alkaline pH were very soluble. At pH 10, it showed a high amount of soluble iron.

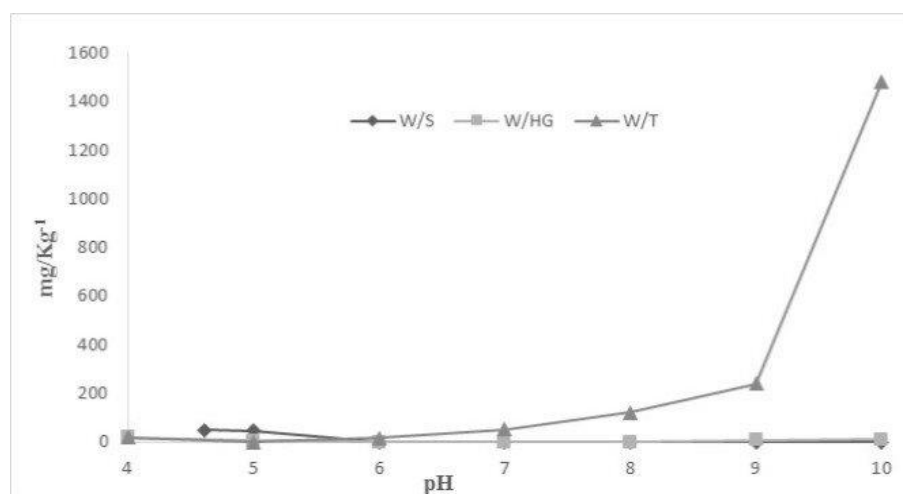


Figure 14: Solubility of iron ore Jerissa (S and HG) and Tamra in the water at different pH (4 to 10) after 24h of interaction.

This outcome can be very relevant since these iron ores could be used as iron natural raw material to be applied like iron fertilizers in calcareous soils where iron deficiency is a crucial nutritional disorder to be solved by applying iron fertilizers.

4. Discussion

Due to the problem of ferric chlorosis and the reduction in plant production yields, the importance of applying ferric fertilizer against this problem in carbonate soils becomes a necessity for the improvement of crop yields and the development of economy. The aim of this study is to obtain a preliminary assessment of both iron ores from Jerissa and Tamra mines to be used as iron fertilizers in agriculture. For that, full physicochemical characterization was done. Soluble iron and extractable iron were determined to estimate the reactivity of these raw materials in soil solution.

Chelating / complexing agents are compounds, mainly polyaminocarboxylic acids, capable of keeping iron soluble; in order to avoid precipitation of iron in the form of insoluble hydroxides due to the high stability of the chelate or iron complex formed (Lucena, 2009). The iron solubility/mobilization rate in the

different formulations depends on: 1) the efficiency and stability of the chelating / complexing agent used in each solution (phenolic, non-phenolic and organic acid), 2) the composition and structure of iron ore (Siderite, hematite / goethite, limonite) and 3) the pH of the solution (acid or basic).

The large differences in extraction efficiency of the agents chelating/complexing are related to pH (acid, neuter or basic), we show that the iron ore Jerissa (S and HG) were extracted at low pH (4 and 5) by the majority of ligands. The iron ore Tamra was mobilized at pH > 7 with the different type of agents.

First, for the iron ore of Tamra characterization, we note that iron exists in the amorphous state and it was in association with clay and silt. The Tamra iron ore which has an initial acid pH (5) has shown enormous extractability with all types of agents (phenolic, non-phenolic and acid) in a wide range of alkaline and ultrabasic

pH region. However, poorly soluble and extractable at acidic pH (4 and 5) may be due to their structure and physicochemical characteristics. At pH superior at 7 the iron concentration in solutions prepared with iron ore Tamra increases for each unit increase of pH.

At pH 7.5 the iron extractability of Tamra is considered as high to average with the ligands. Tamra iron was reacting positively with low molecular weight organic acid (LMWOA). Citrate seem to be very efficacy in extracting iron with a highest amount than all agents as it has been demonstrate by strome 2001 and 2005. Ferric citrate complexes play a major role in iron solubilization, transport and utilization in animals and plants (Milewska, 1988). According to Timberlake (1964), Citric acid, an R-hydroxy tricarboxylic acid, forms a series of stable complexes with Fe (III) ion in aqueous solution over a very large pH range (2-9), thus preventing hydrolysis of ferric ion and formation of insoluble hydroxides/oxides at physiological pH. Besides Oxalate, polycarboxylic ligand, are more efficacy than malate that is it confirmed by strome et al., 2005. Either Humic substance solubilized a good amount of iron ore Tamra (Ciesh et al., 2016). The complexes gluconate and hyptagluconate studied in this experimental assay maintain also Fe soluble in solution. The percentage of Fe that remains in solution is in good agreement with the data obtained by Islas et al. (2019) due to the presence of a wide variety of functional groups. According to Lucena et al., 2008; Rodríguez-Lucena et al., 2010a and b; López-Rayó et al., 2015, 2019, non- phenolic agents (IDHA, EDDS) maintain a good amount of Fe chelated in solution at high pH. The biodegradable chelating agents can be good alternatives to the traditional agents. Then, the most stable phenolic agent (HBED) solubilize the iron from iron ore Tamra. In addition, the later it was soluble in water at pH 7.5 and the pH superior to seven.

The results of solubilization of Tamra iron in the second experiment along pH interval shown that the values of iron concentration of IDHA/Fe (T), Citrate/Fe (T) and HS/Fe (T) were very low at acid pH values but increased at pH above 7. HBED with iron ore Tamra was mobilized more iron when the pH increase from 4 to 10. The order of ligands of extractablign iron are IDHA, Citrate, HS then HBED.

For the iron ore Jerissa, at 7.5 pH the solutions prepared with the two samples S and HG were shown an obvious difference in effectiveness between the agents chelating/complexing. At pH 7.5, the non-phenolic EDDS and IDHA being the most effective acid in mobilizing Fe cation (Lucena et al., 2008; Rodríguez-Lucena et al., 2010b González et al., 2007; Rodríguez-Lucena et al., 2010a) from siderite and hematite/goethite followed by the organic acid (citrate) that dissolves a high amount of iron from iron carbonate and oxy hydroxide iron . Complexes agent as gluconate and lignosulfonate (HS) (Benedicto et al., 2011, Gangloff et al., 2006; Akay and Kaya, 2007) , have shown promising a well results that mobilize the iron in solution with mediocre content .With siderite, hyptagluconate, oxalate, malate and water indicate a negative results that is no extractable and soluble iron in solution. However, with HG at pH 7.5 only malate and water did not maintain extractable and soluble iron in aqueous solution. The presence of a strong ligand is important because of adsorption and because it provides the driving force of the dissolution process.

The second experiment with acid and basic pH, we showed more information and interpretation about mobilization of iron ore Jerissa. The similarity between the low values obtained for the iron extractability by IDHA and citrate ligands from siderite and hematite/goethite is interesting at different pH (4 to 10). The more stable phenolic agent HBED was work very well with siderite at pH 4 and 5 with a high percent but it is very low at basic pH .These results are in good agreement with López-Rayó et al. 2009 and Nadal et al. 2009 . Lignosulfonate (HS) was mobilize iron ore Jerissa (S and HG) at pH 8 and 9 with low percent than HBED.

5. Conclusions

Jerissa ore was characterize by dominance of carbonate minerals with a strong crystallization of iron. Moreover, the fine structure of the particles was influenced on porosity between grains (low % of void). The iron ore of Tamra shows the absence of calcite with a dominance of the quartz and clays with different types and morphology. Due to their complexity in structure and composition, iron ore Tamra was registered a large specific surface area and highly macroscopic pore. All chelating agents extract Fe from iron ore Tamra with several content depends to pH and ligand stability. The highest amount of iron from ore Tamra extracted by organic acid (citrate) at pH superior to seven while the most content chelated from iron ore Jerissa by phenolic ligands HBED at pH 4. The solubilization rate depends on the solid phase (siderite, hematite and goethite, limonite) and the agents chelating/complexing that dissolves iron in aqueous solutions.

Tamra iron ore can be chosen as a very good candidate to be used as natural raw material to be proposed to either to be used as a natural iron fertilizer in alkaline soils due to its good behavior in scenarios similar to calcareous soils or to be used as natural raw in iron fertilizer formulations.

Conflicts of Interest: The authors declare no conflict of interest.

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