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THE ROLE OF MINERAL AND ORGANIC FERTILIZERS AND THEIR INTERACTIONS IN THE MINERAL TRANSFORMATIONS OF CARBONATE MINERALS ON THE *ZEA MAYS* L. AND *HELIANTHUS ANNUUS* L.

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Abstract

A plastic pots experiment to study the effect of organic fertilizer, mineral fertilizer and humic acid and their overlap on the presence of carbonate minerals in both of the rhizosphere and bulk soils during the periods of plant growth (40 and 100) days from planting to maize and (30 and 90) days from planting to sunflower, was conducted. This is in addition to a comparative study of the effect of the two plants' rhizosphere on the proportions and types of carbonate minerals. The experiment was designed according to the complete random design (C.R.D). Mineral fertilization treatments included 250kg.N.h^{-1} for yellow corn 160kg.N.h^{-1} for the sunflower, which are symbolized by the symbol (M). The organic fertilization (poultry waste) was applied at the level 10tons h^{-1}, which is symbolized by the symbol (O), for both plants. Humic acid was applied at the level 450kg.N.h^{-1} that is symbolized by the symbol (H) for both plants. Yellow corn and sunflower seeds were planted in pots. X-ray results present the prevalence of calcite and dolomite in the study soil. The results present a decrease in the intensity of the special diffraction of calcite metal after 100 days of planting. This indicates the occurrence of solubility of this mineral in the yellow corn rhizosphere. That is, mineral fertilization resulted in a decrease in the intensity of the calcite mineral and its intensity varied from one treatment to another. The mineral dolomite was distinguished by its non-sharp peak and its intensity also varied from one treatment to another according to the growth times. The O, H and MHO treatments were the most influential on this mineral. The treatment MHO increased the intensity of this metal and turned its top to a sharp top. As for the percentages of carbonate minerals, there was a decrease in the percentage of calcite metal in all treatments except for the organic fertilization and MHO treatment. The ratio of dolomite minerals decreased with all treatments except for the treatment of mineral fertilization in the yellow maize. As for the sunflower rhizosphere, it is found that there is an increase in the percentage of calcite mineral, except for mineral fertilization and organic fertilization treatments. The percentage of dolomite increased with all treatments except for the treatment of fertilization with humic acid. The arrangement of carbonate minerals in the rhizosphere of both plants was in the following order: Calcite> Dolomite> Magnesite> Cedrite. The studied carbonate minerals were in higher percentages at the yellow corn rhizosphere compared to the sunflower rhizosphere. There was a variation in the percentage of carbonate minerals. These variations indicate that the plant type has a major role in the formation of carbonate minerals and their types and that the type of fertilization had an effective role in dissolving, depositing and forming carbonate minerals on the other hand.

Key words: mineral tests, rhizosphere, carbonate minerals, calcite, dolomite.

Introduction

Carbonate minerals in the rhizosphere of the plant are very important. Wilding, (1987), in a study of forest soils, developed a model to quantify carbonate using the infrared spectrum group and refracted X-ray diffraction. Noting that the origin of forest soil material was newly formed and the presence of carbonate minerals in large quantities there has negative effects, especially on the cation exchange capacity (CEC). This is due to its encapsulation of clay granules and silt, which reduces the cation exchange values, Al-Zubaidi, (1989); Hussein M. Khaeim, *et al*., (2019). Many chemical and physical measurements that stress the necessity of removing carbonate minerals were adopted. Among these measurements are tissues and mineral analysis. The researchers were keen to completely isolate carbonate

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minerals without affecting other properties, especially mineral ones.

There are several methods to buffer the carbonates, but the most important ones are done with hydrochloric acid and sodium acetate. Latif, (2016) found that the best method for removing carbonate minerals without affecting their mineral properties was the treatment of HCl in his study using three soil parameters with a high content of carbonate minerals in the Tilkiv region are standard HCl acid (0.2). The second treatment was the method of sodium acetate with a degree of reaction 5 and compared with the comparison treatment, which was considered the third treatment. Ayers and Westcot, (1985) noted that the melting and precipitation of carbonate minerals is affected by the quality of irrigation water, depending on the effectiveness of calcium, magnesium, carbonate and bicarbonate. Carbonate minerals are diverse and there are more than 290 minerals scattered in different soils, but the predominant ones are cassalite and dolomite, al-Mashhadani, (2008); Baker D. Aljawasim, *et al*., (2020). Calcite and dolomite are the most prevalent and found in calcareous soils.

In Iraqi soil, the calcite is the largest percentage, which is close to 90-95%, while the dolomite and calcite-bearing magnesium constitute 10% of the carbonate minerals, Al-Qaisi, (1999a); Khaeim, H.M. *et al.,* (2019). The soil content of carbonate minerals is one of the criteria that can have an impact on soil properties. Dregne, (1976) present that the source of carbonate minerals in the soil is aerobically deposited deposits in the form of particles of calcium carbonate or calcium salts that interact with CO_2 in the soil to form carbonate minerals, or by carbonate dissolved in groundwater near the surface of the soil, or through the mineralization of plant residues, or by sediments from runoff water or from irrigation water. Al-Kubaisi, (1986) showed that there is a high percentage of carbonate minerals in the soil in the form of single or mixed minutes with the soil or coated with minute clay or fine silicate and this may affect the process of decomposition of the organic matter or the process of staging, Khaeim, H.M. *et al.,* (2019). Jarallah, (2000), in his study on the sediments of the Tigris and Euphrates rivers that the percentage of carbonate minerals in the seasons of the soils of the study took the following order for the deposits of the Euphrates: Alluvium < coarse clay <sand< soft clay. As for the deposits of the Tigris River, I took up the sand < silt<coarse clay> fine clay.

The percentage of carbonate minerals in the clay separator with a fine and coarse particle represents the effective carbonates. Examining the soft sections of the sand separation of both deposits, it was found that the carbonate minerals were present in the form of separate articulations or materials linking the soil articulations and the carbonate articulations were distinguished by being white mixed with red or black color, Khaeim, H.M., (2013); Al-Baldawy *et al*., (2019).

This study aims to investigate the effect of the mineral and organic fertilizing type and their overlap in the presence of carbonate minerals during the growth periods 40 and 100 days and 30 and 90 days from planting for maize and sunflower plants, respectively, as well as to compare the effect of these plants' rhizosphere on fixation of carbonate minerals and their types, Hussein M. Khaeim *et al*., (2020).

Materials and Methods

This experiment was carried out in the canopy of the Department of Soil Science and Water Resources at the College of Agriculture, University of Qadisiyah- Iraq. The soil was brought from the extension station in Nuriya-Diwaniyah, which was air-dried, milled and sifted through a sieve with a diameter of 4mm. 20kg dry soil was placed in each pot and prepared for planting. Seeds of yellow corn (*Zea mays* L.) species of (DKC 6120) and sunflower seeds (*Helianthus annuus* L.) were plantedon the 13th of July 2018 in potted by placing 5 seeds per each. Fifteen days after planting, they were rugged outto a single plant in each pot.

Fertilizers were applied before planting. Potassium sulfate fertilizer 50% K_2O was applied at the level 100kg.K2O.h^{-1}, triple superphosphate fertilizer at the level of 200kg.h^{-1} and urea fertilizer N 46% at the level 250kg.N.h^{-1} were applied for the yellow corn. Potassium sulfate fertilizer K_2O, at a level 80kg.K_2O.h^{-1} and triple superphosphate fertilizer at the level of 80kg.h^{-1} were applied for sunflower plants. Urea fertilizer N 46% at a level 160kg.N.h^{-1} was applied 15 days after planting and the second 30 days after the first application of N to the yellow corn and sunflower plants. Sesamia cailica, the corn stalk borer, was controlled using the granular (diazinon) pesticide, 10% effective material, given to the growing peaks of plants 20 days after germination. The process of hoeing and weeding was done manually in order to get rid of growing bush plants with the yield for each treatment of the yellow corn and sunflower plants whenever needed. Irrigation was carried out when the soil water reached 50% of the field capacity and according to the plant's need, Jeber, B.A. and Khaeim H.M., (2019).

A sample of the soil was taken before planting, dried aerially and crushed with a plastic mallet and passed through a sieve with a diameter of 2mm (holes). Some physical and chemical properties were estimated by the methods mentioned in Jackson, (1958); Black, (1965) and

Table 1: Chemical and physical properties of the soil before planting.

Trait		Value	Unit	Reference
Reaction Degree (pH) (1:1)		7.6	-	Page *et al.*, (2982)
Electrical Conductivity (EC) (1:1)		3.42	DesiSmens.M^{-1}	
Cation exchange capacity (CEC)		23.73	Cml.charge. kg^{-1}.soil	Savant, (1994)
Carbonate minerals		230	g.kg^{-1}	Page *et al.*, (2982)
Organic matter		11.37		Black, (1965)
Cationic dissolved ions	Ca^{2+}	25.45	Cml.charge.L^{-1}	Page *et al.*, (2982)
	Mg^{2+}	13.44		
	Na^{1+}	40.58		Jackson, (1958)
Negative dissolved ions	SO_4^{2-}	17.95		Black, (1965)
	HCO_3^{1-}	16.8		Jackson, (1958)
	CO_3^{-2}	Nill		
	Cl^-	41.56		Jackson, (1958)
Available Nitrogen	N - NH_4^+	22.18	Mg. kg^{-1}	Black, (1965)
	N - NO_3^-	19.33		
Available phosphorous		16.30	Mcg.m^{-1}	Page *et al.*, (2982)
Available potassium		164.40		Black, (1965)
Bulk Density		1.36		
Soil Separators	Sand	270	g.kg^{-1}	
	Loam	540		
	clay	190		
Texture type		Silt Loam		

Page and others, (1982) as shown in table 1. Mineral analysis (XRD) of the rhizosphere was performed during plant growth periods after 40 and 100 days after planting for yellow corn and 30 and 90 days after planting for sunflower, as mentioned in Page and others, (1982). The following treatments were taken to conduct the mineral analyzes:

1. Control Treatment (C)
2. Organic Fertilization (O)
3. Humic acid (H)
4. Mineral fertilization (M)
5. Organic, mineral and humic acid fertilization (MHO)

Results and Discussion

Figs. 1-10, present the x-ray diffraction of the soil of the yellow corn crop during the growing periods 40 and 100 days after planting. Figs. 11-20, present the X-ray diffraction of the sunflower plant's rhizosphere appears during the growth periods 30 and 90 days of cultivation. Calcite and dolomite minerals have been studied through these diffractions because of their importance of these two minerals and because they constitute the largest percentage of carbonate minerals in Iraqi soil, as well as their importance in precipitation and adsorption of elements and influence on the properties of the soils, Al-Qaisi, (1989a); Alawsy *et al.,* (2018); Al-Mashhadani, (2008) and Zunbul, (2005). Calcite can be diagnosed through X-ray diffraction 3.04, 2.39 and 2.10, the anstrum represented by the first, second and third diffraction, respectively.

It was possible for dolomite metal to cheapen it through diffraction of 2.89 inches. The diffraction showed a clear contrast between plant growth times and different treatments. It appears clearly in the growth period 100 days for the yellow corn and 90 days for the sunflower when compared with the periods 40 and 30 days for the yellow corn and sunflower plants, respectively. There was also a discrepancy between the studied parameters, especially in the severity of the diffraction of these minerals. Calcite appeared through the first diffraction 3.04, an anstrum clearly marked with a sharp peak. The low intensity of this diffraction in the comparison treatment after 100 days may be due to the physiological activities and biological secretions of plant roots as well as their respiration, which causes the processing of carbon dioxide. Thus, the formation of carbonic acid causes dissolving these minerals.

The applied treatments lead to increased plant growth and increase the effectiveness of the roots as mentioned above treatment (M) in addition to the effect of these transactions as a source of magnesium. The preparation of this element leads to the inhibition of the formation of calcite metal with the treatments of (O and MHO), Al-Mamouri, (2012) or to its acid effect, which has a fundamental role in dissolving carbonate minerals, especially calcite metal with the treatment (H).

The x-ray diffraction figures of the yellow corn plant

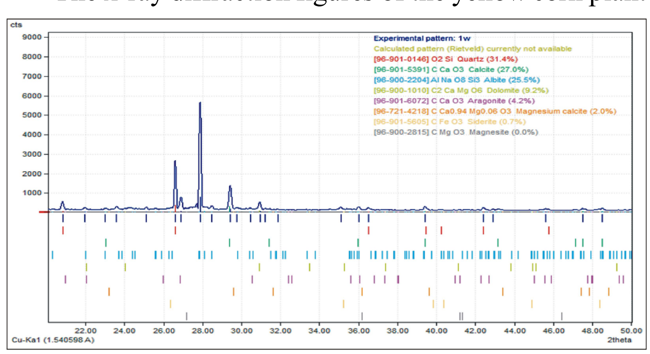

Fig. 1: X-ray diffraction of the control treatment for maize rhizosphere after 40 days of planting.

1-10 present that the dolomite was characterized by having a non-sharp (wide) tip. Its intensity varied from one treatment to another according to the studied growth periods and it was variable. This was evident by the treatment (M) of figs. 3 and 4, that showed an increase in the diffraction intensity of this mineral from approximately 200 to about 2000. This increase may due to an increase in the absorption of calcium from the growth environment as a result of increasing plant requirements for this element and thus increasing the

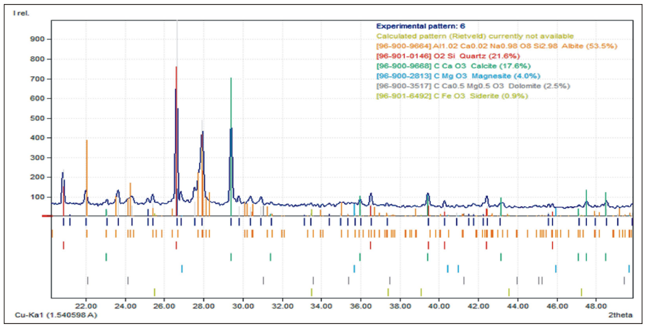

Fig. 2: X-ray diffraction of the control treatment for maize rhizosphere after 100 days of planting.

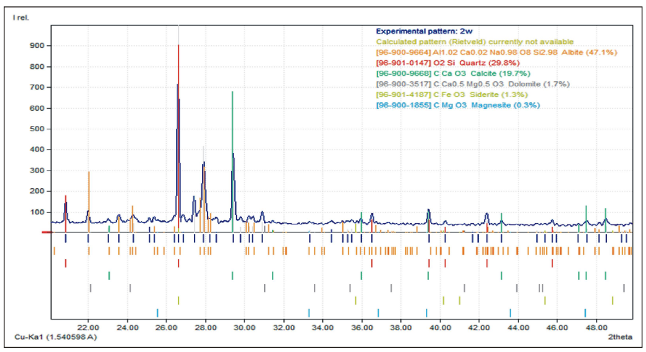

Fig. 3: X-ray diffraction of mineral fertilization for maize rhizosphere after 40 days of planting.

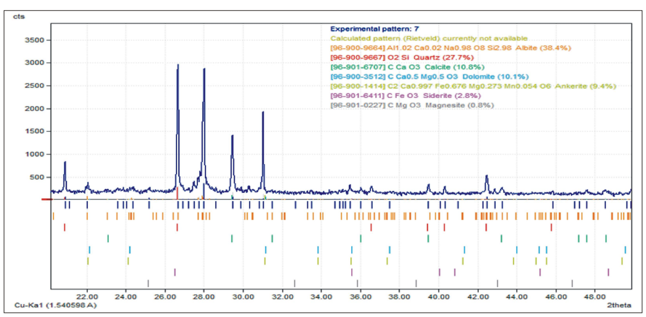

Fig 4: X-ray diffraction of mineral fertilization for maize rhizosphere after 100 days of planting.

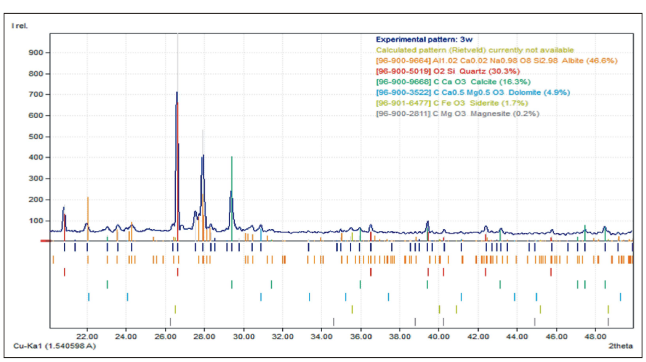

Fig. 5: X-ray diffraction of organic fertilizer for maize rhizosphere after 40 days of planting.

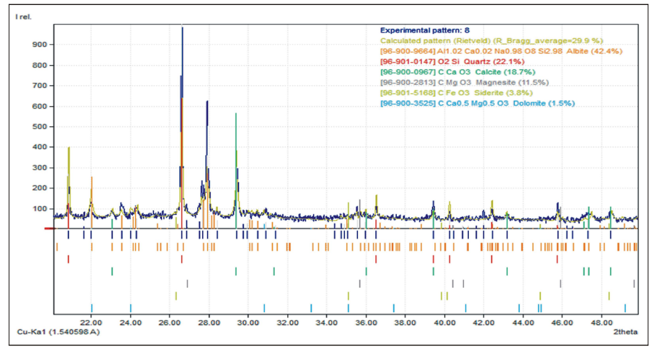

Fig. 6: X-ray diffraction of organic fertilizer for maize rhizosphere after 100 days of planting.

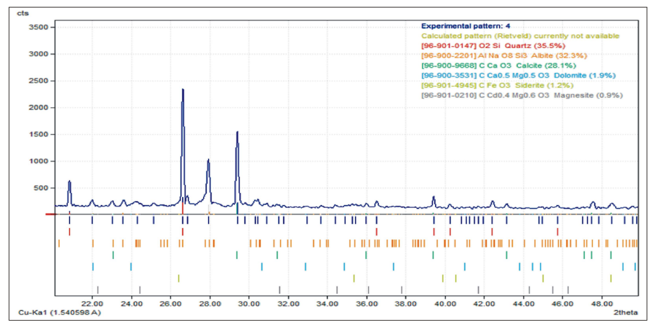

Fig. 7: X-ray diffraction of humic acid for maize rhizosphere after 40 days of planting.

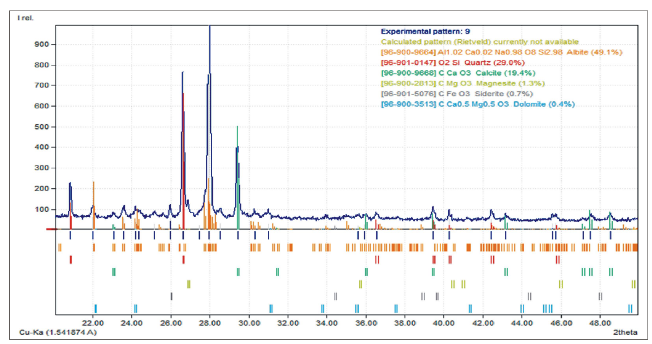

Fig. 8: X-ray diffraction of humic acid for maize rhizosphere after 100 days of planting.

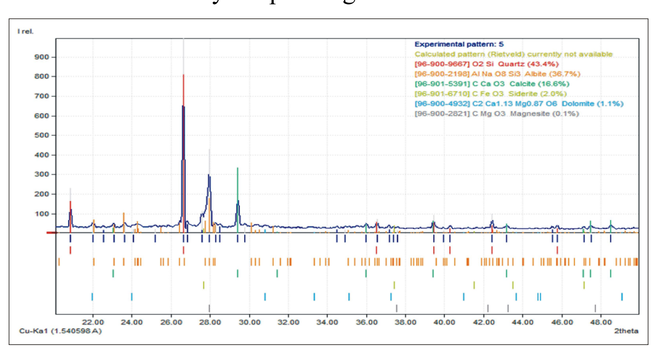

Fig. 9: X-ray diffraction of MHO overlap treatment for maize rhizosphere after 40 days of planting.

concentration of magnesium in the solution, which causes an increase in its concentration and thus radiating the solution with it and depositing it in the form of dolomite mineral as well as the role of irrigation water in increasing its concentration in the soil. This is consistent with that of Ayers and Westcot, (1985) observed in their study

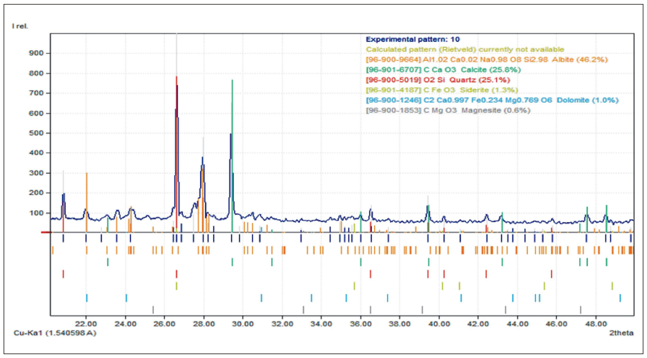

Fig. 10: X-ray diffraction of MHO overlap treatment for maize rhizosphere after 100 days of planting.

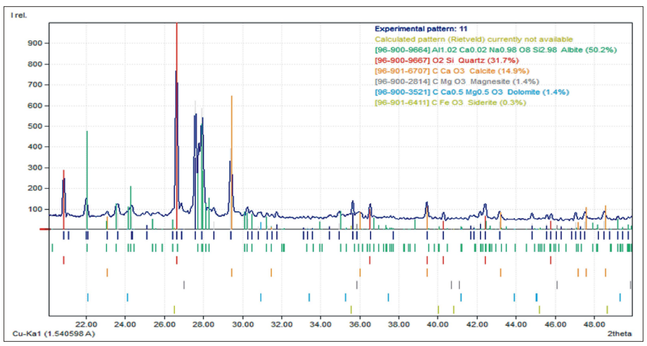

Fig. 11: X-ray diffraction of MHO overlap treatment for maize rhizosphere after 100 days of planting.

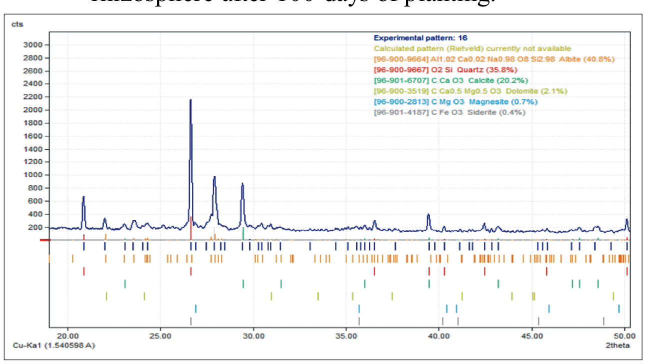

Fig. 12: X-ray diffraction of the control treatment forsunflower after 90 days of planting.

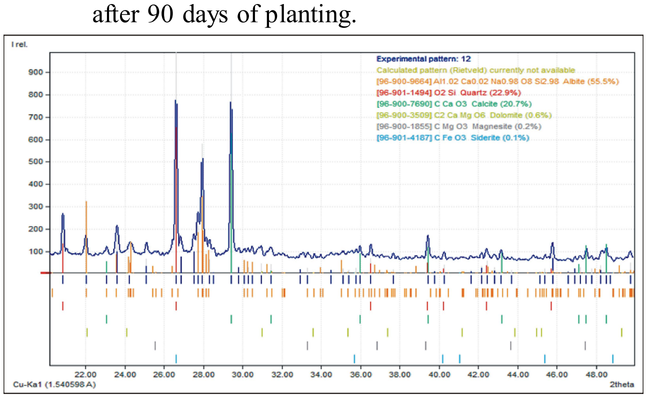

Fig. 13: X-ray diffraction of the mineral fertilizer for sunflower after 30 days of planting.

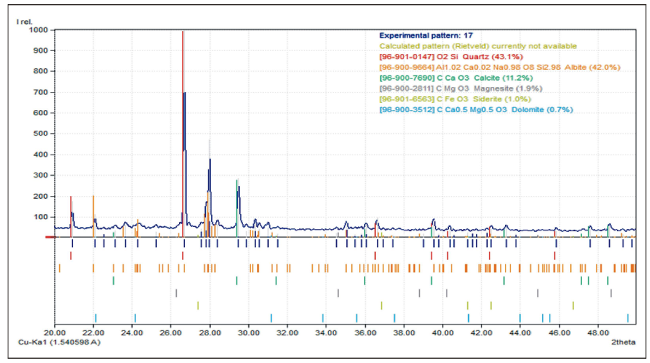

Fig. 14: X-ray diffraction of the mineral fertilizer for sunflower after 90 days of planting.

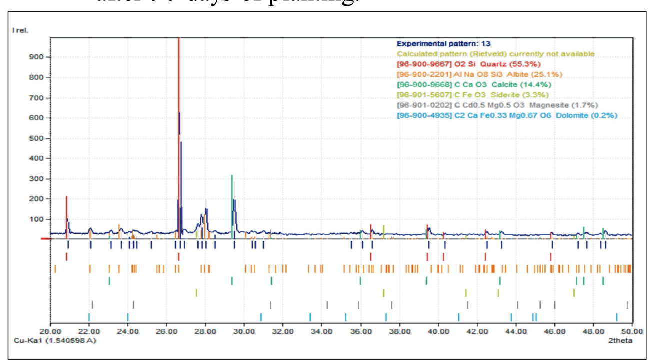

Fig. 15: X-ray diffraction of the organic fertilizer for sunflower after 30 days of planting.

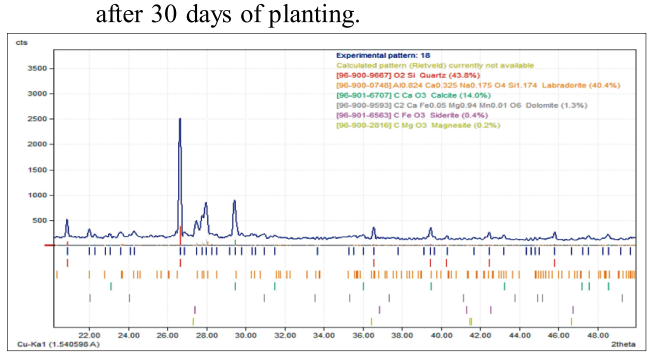

Fig. 16: X-ray diffraction of the organic fertilizer for sunflower after 90 days of planting.

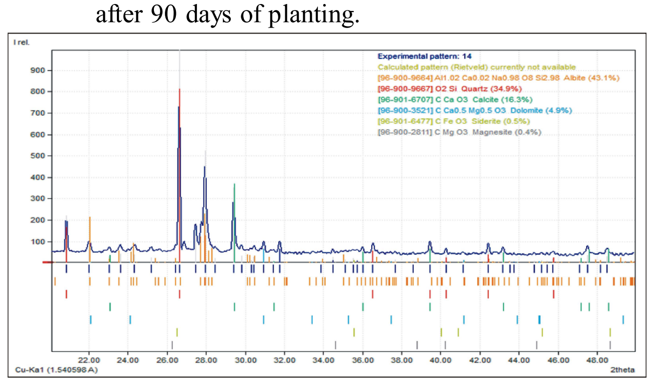

Fig. 17: X-ray diffraction of the humic acid for sunflower after 30 days of planting.

that the melting and precipitation of carbonate minerals is affected by the quality of irrigation water, depending on the effectiveness of calcium, magnesium, carbonate and bicarbonate.

Most of the studies mentioned or related to this issue were very few and do not indicate the nature of the formed carbonate minerals. The treatment of (O, H and MHO) had an effect on this mineral, as the top of the metal was wide at the 100 day period of cultivation and that was due to the effect of these acidic treatments and thus the weathering and melting of this mineral forms 19-24.

X-ray diffraction of the sunflower plant shapes represented in the figs. of 11-20 that showed the presence of calcite mineral, which was possible to cheapen it through diffraction 2.10, 2.39 and 3.04 of the anstrum represented by the first, second and third diffraction, respectively. The dolomite metal diagnosed with diffraction through 2.89 inchstrum. The control treatment showed an increase in the intensity of the two minerals at the 90 day period of planting. This may be due to an increase in the calcium and magnesium ion concentration with the time added with irrigation water Ayers and Westcot, (1985) and accumulated over time as a result of the lower requirements of this plant for these two elements, figs. 11 and 12. Mineral fertilization (M) that represented by figs. 13 and 14 present a decrease in the strength of the calcite mineral. This may due to an increase in the growth of the root system and thus an increase in vital activities and an increase in the production of carbon dioxide, thus the formation of carbonic acid, which dissolves this mineral occurs.

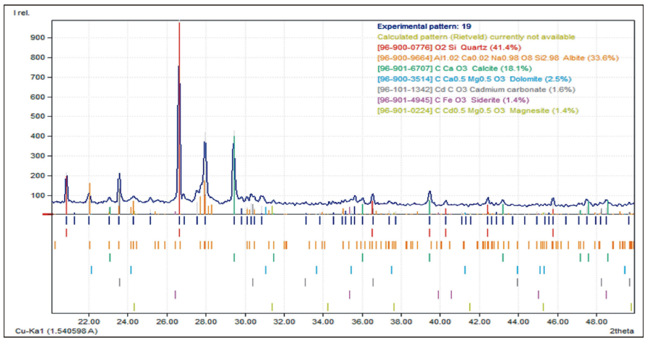

Fig. 18: X-ray diffraction of the organic fertilizer for sunflower after 90 days of planting.

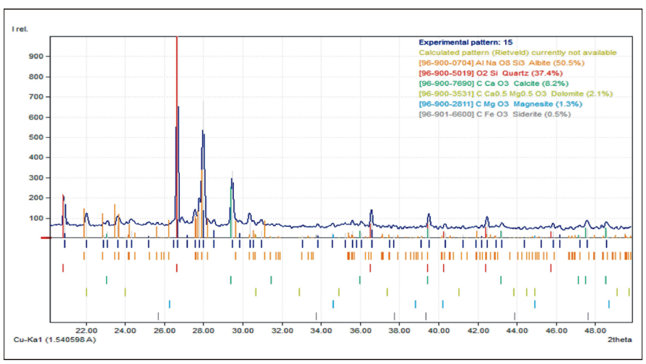

Fig. 19: X-ray diffraction of the MHO overlapfor sunflower after 30 days of planting.

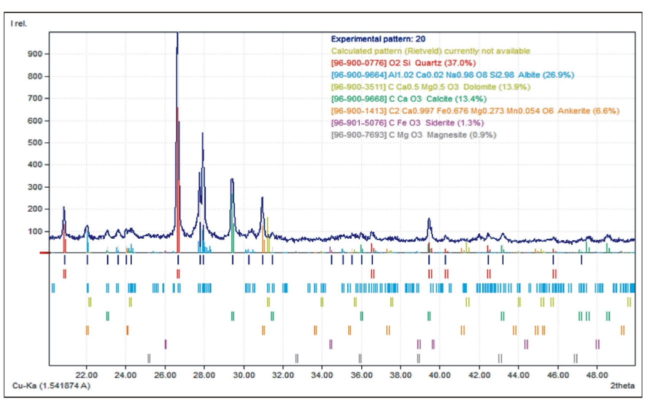

Fig. 20: X-ray diffraction of the MHO overlap for sunflower after 90 days of planting.

The treatments (MHO, H, O) represented by figures 15-20 of the X-ray diffraction showed that there is a variation in the intensity of the calcite mineral from one treatment to another. This mineral was a sharp top with all treatments. The dolomite also varied from one treatment to another and a change in its top appeared and was of a wide tip, figs. 15-18. As for the treatment, MHO increased its intensity and turned into a sharp peak. This is due to the increase in the concentration of calcium as a result of its application with the organic materials and the result of irrigation and its accumulation with increasing time, which increased the formation of this mineral forms, figs. 19 and 20. These changes indicate the different growth environment and plant requirements and the effect of different treatment in the soil pH, which all lead to the formation of different minerals from carbonates, depending on these factors.

The results regarding dolomite indicate that this mineral is not dolomite, but rather a calcite bearing magnesium according to what Al-Kaysi, (1983) found when studying the nature of the mineral composition of some Iraqi soil. Its percentage increases at the reversing of the dolomite, because the dolomite is vulnerable to lose and washing due to weathering factors, while it cannot be deposited in the soil secondary. On the contrary, the magnesium-bearing calcite mineral that can be deposited secondary when increasing the soil solution content of magnesium. This is consistent with what Larsen and Chilingar, (1979) indicated that the dolomite present in the soil must be a primary for not depositing it secondary. It also agrees with Gheber and Arnaud, (1983) that the calcite mineral is present in all soil separations, while the

Table 2: Percentage of minerals dominance in soil culture treatments after 40 days of the planting of maize plants.

Treatment	Calcite	Dolomite	Sidrite	Magnesite
Control	27.0	9.2	0.7	0.0
Mineral fertilizer	19.7	1.7	1.3	0.3
Organic fertilizer	16.3	4.9	1.7	0.2
Humic acid	28.1	1.9	1.2	0.9
Overlab MHO	16.6	1.1	2.0	0.1

dolomite did not appear in the soil separator. Leslie and Barak, (2000) concluded that there was no evidence of secondary dolomite precipitation when using saline solutions ($NaHCO_3$, $MgCl_2$ and $CaCl_2$) and in different proportions of Ca Mg / (4:1, 2:1 and 1:1).

Tables 2 and 3 present the percentages of carbonate minerals in the yellow corn plant rhizosphere 40 and 100 days after planting. These values are taken from the x-ray diffraction, shown in figs. 1-10. The results showed the melting and re-precipitation of carbonate minerals. It noted that a decrease in the percentage of calcite minerals in all treatments except for the treatment of organic fertilizing (O) and overlap fertilization (MHO). This may due to the processing of these two treatments as the calcium ion and thus increase its concentration of the soil solution and then it precipitated. As for the dolomite mineral, its percentage decreased in all transactions except for mineral fertilizing treatment and this is due to the increase in the absorption of calcium ion from the solution and thus the increase in the concentration of magnesium ion, which led to the formation of this mineral. The value of siderite metal increased in all treatments, except for the humic acid (H) and the overlap (MHO) treatments. This indicates the great effect of fertilization with humic acid in melting this mineral and this result was confirmed with the overlapping treatment for the same reason. The valuemanganese metalincreased with all treatments and the carbonate minerals arrangement was taken in terms of their quantities, as follows:

Calcite> Dolomite> Magnesite> Siderite

Tables 4 and 5 showed the percentages of carbonate minerals in the sunflower plant rhizosphere 30 and 90 days after planting. The results showed an increase in

Table 3: Percentage of minerals dominance in soil culture treatments after 100 days of the planting of maize.

Treatment	Calcite	Dolomite	Sidrite	Magnesite
Control	17.6	2.5	0.9	0.0
Mineral fertilizer	10.8	10.1	2.8	0.3
Organic fertilizer	18.7	1.5	3.8	0.2
Humic acid	19.4	0.4	0.7	0.9
Overlab MHO	25.8	1.0	1.3	0.1

Table 4: Percentage of minerals dominance in the treatments of study soils after 30 days of planting the sunflower plant.

Treatment	Calcite	Dolomite	Sidrite	Magnesite
Control	14.9	1.4	0.3	1.4
Mineral fertilizer	20.7	0.6	0.1	0.2
Organic fertilizer	14.4	0.2	3.3	1.7
Humic acid	16.3	4.9	0.5	0.4
Overlab MHO	8.2	2.1	0.5	1.3

the percentage of calcite mineral with all treatments, except with mineral fertilization (M) and organic fertilizing (O). This may be due to the differing requirements of the plant's nutritional requirements and processing from one treatment to another. As for the dolomite mineral, its percentage increased, except for the treatment of humic acid (H), whose value decreased with time. This may due to the progressive acid effect of this treatment and the processing of the hydrogen ion of the solution, which leads to a decrease in the soil pH and thus an increase in the solubility of this mineral.

Regarding siderite metal, its value increased in all transactions except for the treatment of organic fertilization. This may be due to the increase in the growth of microorganisms, considering that the organic matter is a source of its energy, thus increasing its growth and reproduction and increasing its need for the iron ion (which is included in its composition) and thus its attack against this mineral, which led to an increase in its solubility to complete its nutritional requirements. The magnesitemineral percentage decreased except with the treatment of mineral fertilization (M) and the treatment of humic acid (H). This is due to the increase in the absorption of calcium and thus the increase in the magnesium ion in the solution, which led to an increase in its concentration and thus its precipitation as a mineral of magnesite. It confirms this is an increase in the melting of calcite with mineral fertilization and an increase in the solubility of dolomite in the treatment of humic acid. The sequence of carbonate minerals in terms of their quantities was similar to what was found in the yellow corn plant rhizosphere, in the following sequence:

Calcite> Dolomite> Magnesite> Siderite

Table 5: Percentage of minerals dominance in the treatments of study soils after 90 days of planting the sunflower plant.

Treatment	Calcite	Dolomite	Sidrite	Magnesite
Control	20.2	2.1	0.4	0.7
Mineral fertilizer	11.2	0.7	1.0	1.9
Organic fertilizer	14.0	1.3	0.4	0.2
Humic acid	18.1	2.5	1.4	1.4
Overlab MHO	13.4	13.9	1.3	0.9

Conclusion

Based on these results, the studied minerals were in higher percentages in the rhizosphere of yellow corn compared to the sunflower one. There is a variation in the percentages of carbonate minerals between the rhizosphere of the yellow corn and sunflower plants. This indicates that the plant type has a major role in the formation of carbonate minerals. The type of fertilization had an effective role in dissolving, depositing and forming carbonate minerals.

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