



# EFFECT OF IRRIGATION PATTERN ON IRON FORMS AND FREE OXIDES IN RICE SOILS OF MIDDLE EUPHRATES GOVERNORATES

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## Abstract

This study was conducted at the rice research station of the Agricultural Research Office, Ministry of Agriculture in Al- Najaf governorate, Al-Mishkhab District. These stations use two methods to irrigate the rice crop, the first waterlogged soil method, where the soil is flooded with water from the date of cultivation until the date of harvest. While the second method is known as the dry method, where the crop is irrigated every three days by flooding, and followed by a period of drought for three days, and also the process of saturated and drought continues till the middle of the season, then the soil is continuously flooded until harvest. Soil samples were obtained from the cultivated land of rice crop that irrigation with two methods (waterlogged and dry), from two depths of 30 and 60 cm, and on six stages per month during the cultivation period. Moreover, some of the physical, chemical, and mineral properties were estimated, as well as different iron forms were estimated, diagnosed and extracted in the form of totally free iron oxides  $Fe_T$ , Crystalline free iron oxides  $Fe_d$  and Amorphous free iron oxides  $Fe_o$ . The results showed that the values of the concentrations of soluble iron within the depth of 60 cm were higher when compared to their values within the depth of 30 cm and for both soils, waterlogged and dry. The soluble iron ion concentration values were the least affected by the variation of the applied irrigation pattern compared to other iron forms. Moreover, the results showed that the concentration values of exchangeable iron ion within the depths 30 and 60 cm in the dry soil were higher than the values in the two depths mentioned in the waterlogged soil, as the exchangeable forms of the iron ion was the most affected by the variation of the applied irrigation pattern in these soils. Furthermore, the results showed that the content of amorphous free iron oxides  $Fe_o$  was varied according to the applied irrigation system in these soils, as the  $Fe_d / Fe_o$  ratio values in the waterlogged soil exceeded by 2-3 times over its ratio in dry soil. The applied irrigation system has affected these soils in the calculation of  $Fe_T / Fe_d$  ratio, as the mentioned ratio values within the dry soil increased as a result of the succession of the two water logging – drought processes.

**Keywords:** Iron, free oxides, rice soils

## Introduction

Free iron oxides in the soil are in the form of crystalline and amorphous forms and include nine common forms, where the goethite  $FeOOH - \alpha$ , hematite  $Fe_2O_3 - \alpha$ , lipedocrocite  $FeOOH - \gamma$  and maghemite  $Fe_2O_3 - \gamma$  are the most common crystalline forms in soils (Shwertmann and Taylor 1977). (Navrotsky *et al.*, 2008) indicate that in terms of thermodynamics, the goethite mineral is the most stable form when the relative humidity in the soil is more than 70% and it is widely available in the temperate region soils in the form of brown or dark reddish-brown color. While for hematite, it is more common in hot and tropical areas in the form of a light red color, even if it is available in a few forms. Furthermore, (Schwertmann

and Cornell, 2003) stated that iron oxides appear in the soil in several forms: such covers around the surfaces of soil minerals, individually shaped as clay particles and combined with the organic matter, forming complex organic compounds with it. These connections for iron with soil components are affected by prevailing soil formation processes and the surrounding environmental conditions, which resulted in a difference within the distribution over the soil structure. Moreover, it was observed that the distribution of free iron oxides did not take a specific pattern of vertical distribution through the soil pedon because of the differences in the iron content within the crystalline structures of the minerals that carrying it in the soil, as it was found a compatibility between silicate iron and free iron oxides. In Iraq, studies have confirmed that the soil content of these oxides was

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very few. (Al-Taie, 1968) found that the free iron oxides content in limestone soils in Western desert ranges between (0.18 - 0.24%), while in the gypsum soils in the Gazira region it reached (0.5%) and is distributed regularly in the soil structure. (Acebal *et al.*, 2000) indicated that iron oxides considered as one of the major components of several types of soils in the world, these components have effects on chemical and physical properties, including the surface area, exchange capacity of the cation ions CEC, adsorption, aggregate stability AS, etc. Additionally, (Yilmaz *et al.*, 2005) noted that free iron oxides are one of the important factors in aggregate stability in soils. Several studies (Muller *et al.*, 2015; Rout and Sahoot, 2015) were observed the extreme importance of the iron ion in influencing the yield and productivity of rice crop, as the iron ion enters many vital actions of the rice plant, as it participates in influencing the effectiveness of many enzymes, Mitochondria synthesis, photosynthesis, nucleic acid synthesis, protein, and chlorophyll productivity. Therefore, recent studies began to focus on the study of the physicochemical behavior of iron ion in rice farm soils, for its importance in the process of growth and increasing productivity. The soil is considered as the primary source of iron for plants, And that its optimum readiness in a soluble form ( $Fe^{2+}$ ) is necessary to supply the plant with what it needs from the element, especially in the rhizosphere (Bshir *et al.*, 2014; Kim and Guerinot, 2007). (Roychoudhury and Das 2014) observed that approximately 30% of rice farm soils suffer from a lack of iron availability, while approximately 18% of rice farm soils is affected by the high availability of the element, which amounts to toxicity. The reason for this variance in readiness was due to several factors, including heterogeneity in the reduction potential, soil-reaction number pH, and fertilizer status. The variation in the readiness intensity of the iron ion in rice farm soils greatly affects the quality and quantity of the yield, also this variance has led to a reduction of approximately 50% of cereal productivity in some cases, in other cases, agriculture has also failed in its early stages (Rout *et al.*, 2014). (Vose, 1982) stated that during its cultivation, rice needs about 60-300 ppm from iron the concentration. Soils containing concentrations ranging from 10-30 ppm iron considered as soils suffer from a lack of readiness to the element, while the soils with a concentration of iron exceeding 400 - 1000 ppm iron suffers from a degree of toxicity to the element.

## Materials and Methods

### Study locations:

The rice research station of the Agricultural Research Office/Ministry of Agriculture within Al-Najaf governorate/ Al-Mishkhab District, an area of 240 dunums was selected to be a site for conducting the current study.

The mentioned station has cultivated the rice crop since 1970 AD, using two methods of crop irrigation transplanted (waterlogged soil) and dry method within the duration from of cultivation the crop is in mid-June and harvested after mid-November. In the first method, which is the traditional method for rice crop cultivation, where the soil is flooded with water, then the seeds are scattered, while the soil remains flooded with water from the date of cultivation until the date of harvest. The second method, known as the dry method, which is used to increase the efficiency of water consumption, through which the crop is irrigated every three days (by flood), followed by a drought period for three days, and the process of saturated and drought continues till the middle of the season. Subsequently, the soil is continuously flooded with water until harvesting. Soil samples were obtained from all cultivated land of rice crop, which uses the mentioned two irrigation methods (waterlogged soil and dry), with two depths of 30 and 60 cm, and in six stages during the cultivation period, as follows. Before cultivating the rice crops on 23/6/2018, and after one month of cultivation on 23/7/2018 then, after two months of cultivation on August 23/8/ 2018. As well as, after three months of cultivation, on 23/9/2018 and after four months of cultivation, on 23/10/2018, then After five months of cultivation, on 23/11/2018. The particle size distribution of soil was estimated according to (Kilmer and Alexander, 1949) method. While the total content of carbonate minerals and active carbonates, soil PH, electrical conductivity Ec, organic matter, soluble ions and cation exchange capacity CEC was estimated according to the methods mentioned by (Page 1982). Finally, 26 soil samples were collected from depths 30 and 60 cm, which are different in the method of cultivation, and was air-dried, then milled with a plastic mallet, and sifted through a 2 mm diameter sieve.

### Iron oxide extraction in the soil

#### Total free iron oxides ( $Fe_T$ )

Iron in the form of free oxide form was extracted using Citrate-Bicarbonate-Dithionite (CBD) method, according to (Mehra and Jackson 1960) method. Additionally, iron was estimated using an Atomic absorption spectrophotometer with a wavelength of 882 nm.

#### Amorphous free iron oxides ( $Fe_o$ )

Amorphous free iron oxides were extracted for soil samples using a solution of acid ammonium oxalate (pH = 3) according to (Schwertman, 1964) method. Additionally, the extracted iron was estimated by the Atomic absorption spectrophotometer, which represents

**Table 1:** Some chemical and physical properties of the soils under study.

Property	Unit	Comparison		Dry		Waterlogging soil	
		30 cm	60 cm	30 cm	60 cm	30 cm	60cm
Texture	----	sicl	sicl	sicl	sicl	cl	cl
Sand	gm.kg <sup>-1</sup>	182	170	178	183	224	218
Silt	gm.kg <sup>-1</sup>	450	415	432	397	414	412
Clay	gm.kg <sup>-1</sup>	368	415	390	420	372	380
Ca <sup>+2</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0.63	1.115	1.395	1.24	1.527	1.415
Mg <sup>+2</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0.487	0.825	0.979	0.891	1.079	1.004
Na <sup>+1</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	1.4	2.189	2.543	2.308	2.817	2.647
K <sup>+1</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0.035	0.066	0.079	0.071	0.092	0.079
Cl <sup>-1</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0.918	1.536	1.760	1.627	1.975	1.869
SO <sub>4</sub> <sup>-2</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0.220	0.365	0.428	0.382	0.467	0.430
Hco <sub>3</sub> <sup>-1</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0.186	0.290	0.366	0.332	0.393	0.361
CO <sub>3</sub> <sup>-3</sup>	cmol <sub>+</sub> .kg <sup>-1</sup>	0	0.3	0.6	0.5	0.8	0.7
CEC	cmol <sub>+</sub> .kg <sup>-1</sup>	24.9	26.5	25.4	28.8	21.5	20.7
O.M	%	1.16	0.86	1.20	0.90	1.12	0.79
Calcium carbonate minerals	%	328	315	309	293	283	291

the amorphous free iron oxides after its conversion.

#### Crystalline free iron oxides (Fe<sub>d</sub>)

Their proportions were calculated from the difference between the value of total oxides and amorphous oxides.

## Results and Discussion

### Soluble - Fe

The results of Table 2 showed the values of soluble iron concentrations for both depth of 30 and 60 cm in the soil under study, where those values ranged between (0.001, 0.011), (0.002, 0.001) and (0.001, 0.0001) Cmol.Kg<sup>-1</sup> within dry, waterlogged and comparison soils respectively. As well as, results showed that the values of the soluble iron concentrations within the depth of 60 cm were somewhat higher when compared to the depth of 30 cm and for both soils, dry and waterlogged. The increase of the soluble iron concentrations within the depth of 60 cm can be attributed to the effect of the washing factor resulting from the rise in the depth of water on the surface horizon during the water logging duration, which helped wash iron ions to the lower horizons of the soil pedon.

### Exchangeable - Fe

The results of Table 2 showed the values of exchangeable iron concentrations for both depth of 30 and 60 cm in dry, waterlogged and comparison soils, where those values ranged between (0.070,

0.104) (0.048, 0.065) (0.090, 0.108) and (0.086, 0.0116) Cmol.Kg<sup>-1</sup> respectively. It was observed from the results that the values of exchangeable iron concentrations within the depths 30 and 60 cm in dry soil were higher than its value in the two mentioned depths in the waterlogged soil, this increase was due to the oxidation state that the soil is exposed to it during the succession of the water logging and drought processes by the applied irrigation system. As the results of Table 2 also showed that the values of exchangeable iron concentrations recorded at depths 30 and 60 cm within dry soil samples during the first month of planting the crop were 0.057 and 0.095 Cmol.Kg<sup>-1</sup>, respectively. Then it started to increase

gradually in the following months, reaching a maximum by the rate of 0.114 and 0.137 Cmol.Kg<sup>-1</sup> respectively, during the fourth month of planting the crop, after that, those values decreased after applying the water logging irrigation system by 0.073, 0.106 Cmol.Kg<sup>-1</sup>, respectively.

### Not exchangeable iron

It is the iron that is not held by electrostatic forces (Van der waals forces), which resulting from the negative charges of the metal layers and the internal oxides carrying it, and its quantity affected by several factors, including the content and type of metal or oxide, the degree of interaction of the medium, soil texture, surface area, and soil moisture content. The results of Table 2 showed the values of not exchangeable iron concentrations in dry, waterlogged and comparison soils, for the depths 30 and 60 cm, ranged between (0.158, 0.220), (0.145, 0.193), (0.189, 0.200) Cmol.Kg<sup>-1</sup>, respectively. The results indicated that the values of not exchangeable iron concentrations in the dry soil were higher than the values recorded in the waterlogged soil, and this variation in the values of not exchangeable iron within the two soils can be attributed to the differences in some chemical and physical properties between the two soils. In particular, the clay fraction content and the cation exchange capacity of soil where the clay fraction content and the cation exchange capacity within the dry soil were higher when compared to the values recorded in the waterlogged soil as shown in Table 1. Moreover, it also appears that the irrigation system applied within the two soils has greatly affected the transformation of the insoluble form of iron into the two soluble and exchangeable forms.

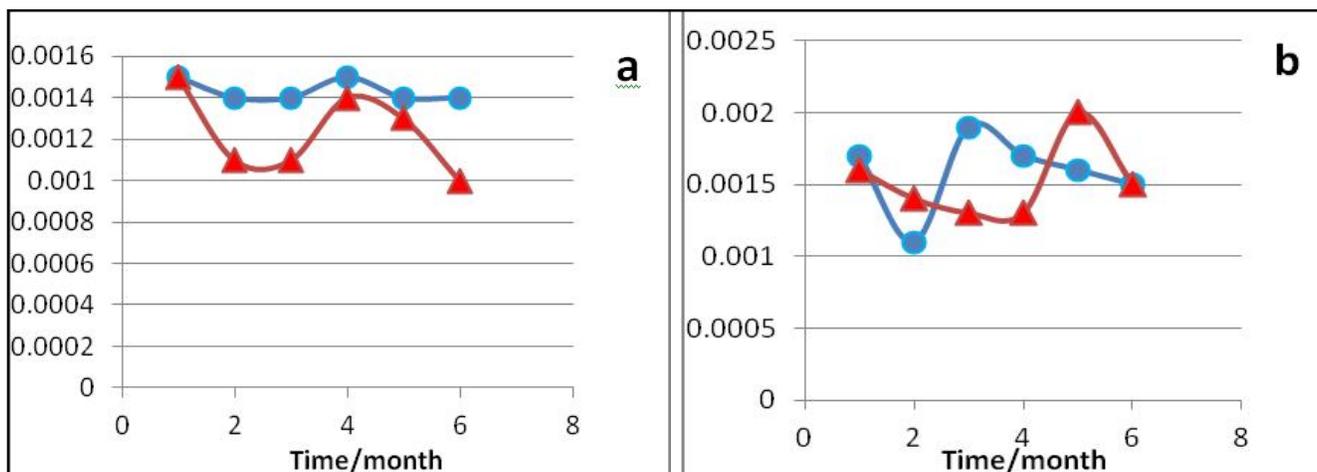
**Total - Fe**

The results of Table 2 showed the values of total iron concentrations for both depth of 30 and 60 cm in dry, waterlogged and comparison soils, where those values ranged between (1.298, 1.750) (1.457, 1.675) (1.296, 1.369) (1.408, 1.567) (1.420, 1.630)  $\text{Cmol.Kg}^{-1}$ , respectively. Furthermore, the results showed that the values of total iron concentrations, in general, were convergent with a slight superiority of those values within the dry soil when compared to the values recorded in the waterlogged soil. However, the general convergence in the values of total iron concentrations in both soils is explained by the fact that the two soils are sedimentary, and formed from the same parent materials. Finally, the total content of the iron ion in them is a result of the product from the parent materials, as well as what is added of iron compounds by fertilization, and the output of this content is what is absorbed by the plant (rice crop)

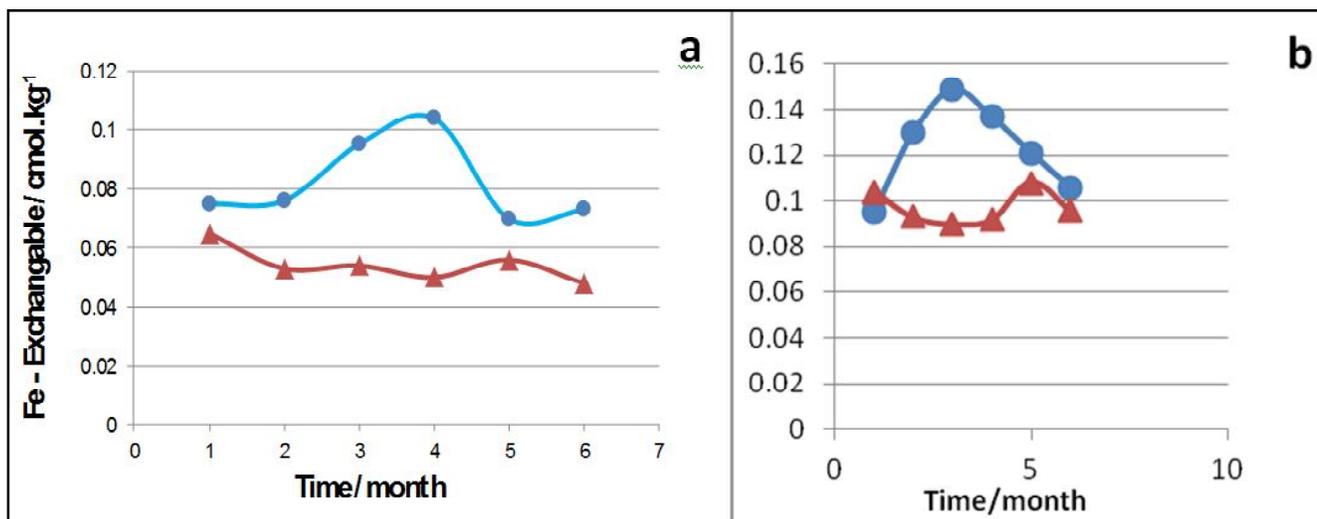
in both soils. In general, the input from the ion and the output from it is one in both soils, and the only difference is the type of irrigation applied on them, which not affect on the total content of iron ion, but, its effect is in the other forms of iron (soluble and exchangeable) which related to the two oxidation and reduction states affected by the irrigation pattern applied in both dry and waterlogged soils.

**Total free iron oxides ( $\text{Fe}_T$ )**

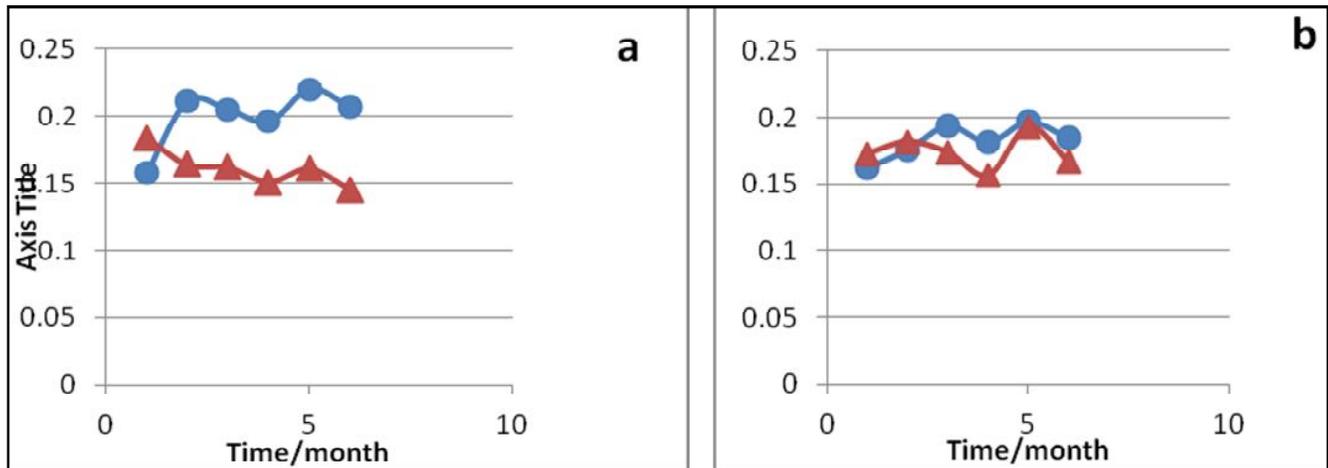
The results of Table 3 showed that the total free iron oxides content in the waterlogged and dry soils and for both depths 30 and 60 cm, ranged between (4.97, 6.37), (5.49 and 7.25)  $\text{g Fe}_2\text{O}_3. \text{Kg}^{-1}$  soil, respectively. The results also showed that the values of total free iron oxides were convergent to each other in all study soils, with a slight superiority for those values within the dry soil compared to the values recorded in the waterlogged soil. The superiority of the total free oxide values within the dry



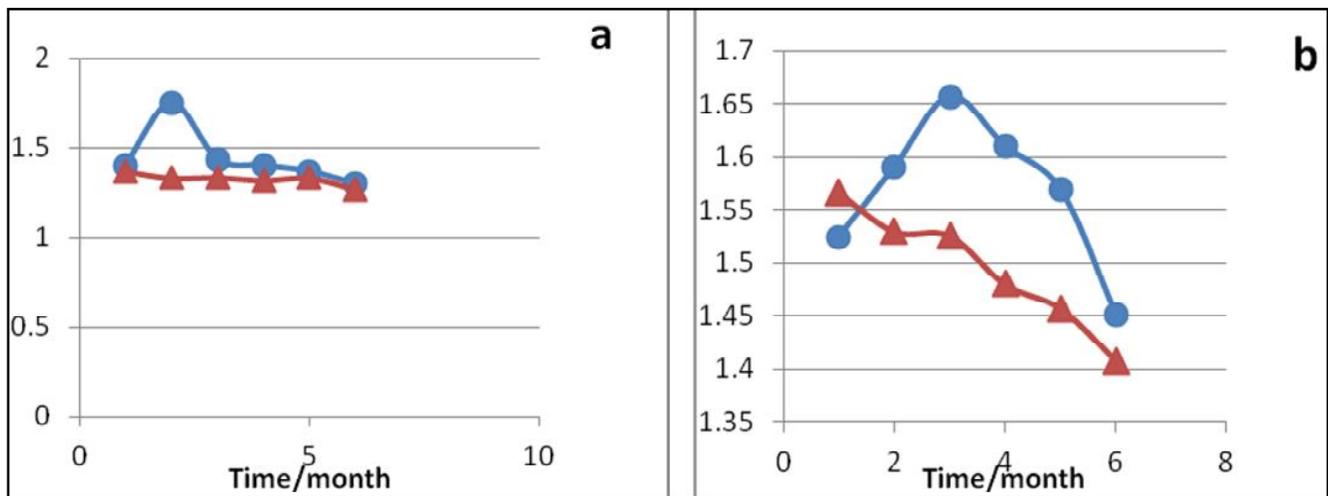
**Fig. 1:** Distribution of soluble iron content in dry (Cercul points) and waterlogged (Triangle points) soils for the two depths 30 cm (a) and 60 cm (b).



**Fig. 2:** Distribution of exchangeable iron content in dry (Cercul points) and waterlogged (Triangle points) soils for the two depths 30 cm (a) and 60 cm (b).



**Fig. 3:** Distribution of non exchangeable iron content in dry (Cercul points) and waterlogged (Triangle points) soils for the two depths 30 cm (a) and 60 cm (b).



**Fig. 4:** Distribution of total iron content in dry (Cercul points) and waterlogged (Triangle points) soils for the two depths 30 cm (a) and 60 cm (b).

soil can be due to the effect of the irrigation pattern applied on that soil, as the sequence state of (waterlogged – drought) affects the sequence of oxidation and reduction, which creates the appropriate conditions for increasing the crystallization of free iron oxides in the soil. (Gasparatos *et al.*, 2006) showed that the succession of oxidation and reduction processes in the soil increases the process of free iron oxides by calculating the ratio of the crystalline iron oxides  $Fe_d$  to the total ratio of free iron oxides in the soil  $Fe_T$ . They found that the percentage of  $Fe_d / Fe_T$  was increasing in soils under the effect of a succession of water logging - drought compared to continuously waterlogged soils, and they attributed this to an increase in the formation and accumulation of free iron oxides in these soils. In confirmation of the results obtained by the current study, the ratio of  $Fe_d / Fe_T$  was calculated within the dry and waterlogged soils and for the depths 30, 60 cm. Furthermore, the results of Table 3 showed that the mentioned percentage values were

convergent in the two soils in the first month of the cultivation process, then it began to change as the irrigation systems continued to be applied in both soils, where the values of  $Fe_d / Fe_T$  started gradually increasing within the dry soil until the end of the fourth month of cultivation (end of applying the successive irrigation system (waterlogging - drought)). The values then begin to decrease to a minimum of (0.82) at the end of the cultivation season (during applying the water logging system). The fluctuation of  $Fe_d / Fe_T$  values within the dry soil can be due to the effect of the successive irrigation pattern (water logging - drought) applied, which created the conditions for increasing the crystallization of free iron oxides in the mentioned soil. While the continuous water logging process that was applied after the end of the fourth month reduced the values of the reduction potential (Eh), creating conditions that were not appropriate for the crystallization process. These results are consistent with what (Essa, 1990) findings during the

**Table 2:** different iron forms in the soil understudy.

	Comparison (Cmol.Kg <sup>-1</sup> )		Dry (Cmol.Kg <sup>-1</sup> )		Water logging (Cmol.Kg <sup>-1</sup> )	
	30	60	30	60	30	60
Soluble Fe	0.0016	0.0018	0.0015	0.0017	0.0015	0.0016
			0.0014	0.0011	0.0011	0.0014
			0.0014	0.0019	0.0011	0.0013
			0.0015	0.0017	0.0014	0.0013
			0.0114	0.0016	0.0013	0.002
			0.0014	0.0015	0.0001	0.0015
Exchangable Fe	0.086	0.116	0.075	0.095	0.065	0.104
			0.076	0.130	0.053	0.093
			0.095	0.149	0.054	0.090
			0.104	0.137	0.050	0.092
			0.070	0.121	0.056	0.108
			0.073	0.106	0.048	0.096
Non exchangeable Fe	0.200	0.189	0.158	0.163	0.184	0.173
			0.211	0.176	0.164	0.182
			0.205	0.194	0.162	0.174
			0.196	0.182	0.151	0.157
			0.220	0.197	0.161	0.193
			0.207	0.185	0.145	0.167
Total Fe	1.423	1.630	1.402	1.524	1.368	1.566
			1.749	1.589	1.329	1.529
			1.434	1.656	1.332	1.525
			1.400	1.609	1.316	1.479
			1.368	1.568	1.329	1.457
			1.297	1.450	1.268	1.407

studying of the behavior of free iron oxides in the soil under the influence of different patterns of water logging and the (water logging – drought) succession. It was found that the process of the free iron oxides crystallization was directly proportional to the pattern of fluctuation of water logging and drought cycles in the

soil, whereas, the continuous water logging process inhibited the crystallization process of these oxides. As for the waterlogged soil, the results of Table 3 showed that the  $Fe_d / Fe_T$  ratio values, and as mentioned previously it was close to the values recorded in the dry soil and during the first month of the rice crop cultivation process, then it started to gradually decrease to settle at the value (0.63 - 0.66) until the end of the cultivation season. The state of stability in the values of the percentage mentioned in the waterlogged soil can be explained through the continuous water logging status during the growing season of rice crop within the mentioned soil lead to reaching the equilibrium state for iron forms according to the rules of thermodynamic equilibrium, which are reflected in the state of crystallization and free iron oxides in the waterlogged soil.

#### Crystalline free iron oxides ( $Fe_d$ )

The results of Table 3 showed the content of crystalline free iron oxides in the study soils, as their value within the waterlogged soil and for the depths of 30 and 60 cm ranged between 3.27 and 5.17 g  $Fe_2O_3.kg^{-1}$  soil, clearly as the results showed that those values were low when compared to their values in dry soil. The reason for this decrease was due to the continuing water logging state of this soil, which led to the continued decrease in

the values of the crystalline iron  $Fe_d$ , and those results were consistent with what (Willett and Wiggins 1980) pointed out when studied the state of crystalline iron oxides  $Fe_d$  on rice farm soil and under two irrigation systems. The first system includes continuously water logging the soil during the growing season while applying

**Table 3:** Concentrations of iron oxides forms in soil understudy.

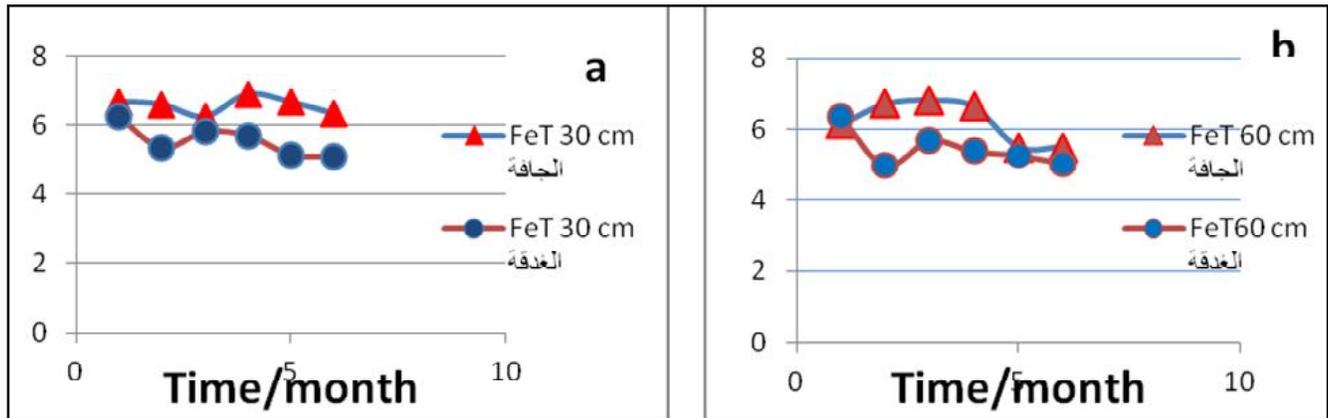
	Depth	Unit	$Fe_T$		$Fe_d$		$Fe_o$	
			Dry (Cmol.Kg <sup>-1</sup> )	Waterlogged (Cmol.Kg <sup>-1</sup> )	Dry (Cmol.Kg <sup>-1</sup> )	Waterlogged (Cmol.Kg <sup>-1</sup> )	Dry (Cmol.Kg <sup>-1</sup> )	Waterlogged (Cmol.Kg <sup>-1</sup> )
1	30	gm.kg <sup>-1</sup>	6.68	6.24	5.60	5.04	1.08	1.20
	60	gm.kg <sup>-1</sup>	6.13	6.37	5.41	5.17	0.72	1.20
2	30	gm.kg <sup>-1</sup>	6.59	5.35	5.83	3.87	0.76	1.48
	60	gm.kg <sup>-1</sup>	6.71	4.97	5.81	3.37	0.90	1.60
3	30	gm.kg <sup>-1</sup>	6.25	5.80	6.61	3.99	0.64	1.81
	60	gm.kg <sup>-1</sup>	6.82	5.68	6.18	3.88	0.64	1.80
4	30	gm.kg <sup>-1</sup>	6.89	5.70	6.29	3.78	0.60	1.92
	60	gm.kg <sup>-1</sup>	6.64	5.38	5.96	3.53	0.68	1.85
5	30	gm.kg <sup>-1</sup>	6.66	5.15	5.92	3.27	0.74	1.88
	60	gm.kg <sup>-1</sup>	5.49	5.26	4.56	3.52	0.93	1.74
6	30	gm.kg <sup>-1</sup>	6.33	5.11	5.40	3.42	0.94	1.69
	60	gm.kg <sup>-1</sup>	5.50	5.03	4.54	3.32	0.96	1.71

**Table 4:** The percentages of iron oxides forms in the soil under study.

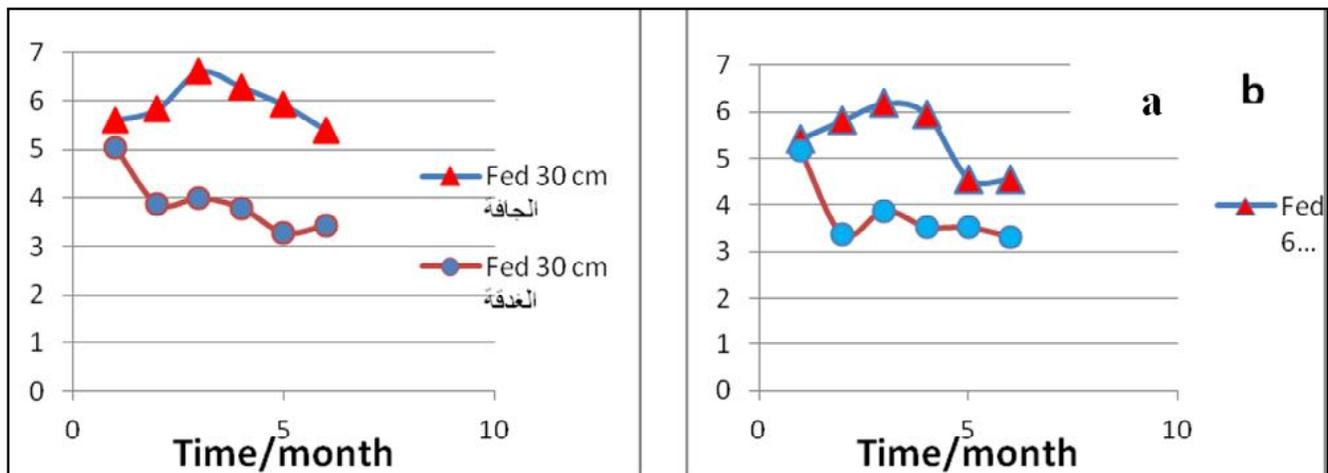
	Depth	Fe <sub>o</sub> /Fe <sub>d</sub>		Fe <sub>d</sub> /Fe <sub>T</sub>	
		Dry	Waterlogged	Dry	Waterlogged
1	30	0.19	0.23	0.83	0.80
	60	0.13	0.23	0.88	0.81
2	30	0.13	0.38	0.88	0.72
	60	0.15	0.47	0.86	0.67
3	30	0.10	0.45	1.05	0.68
	60	0.10	0.46	0.90	0.68
4	30	0.10	0.50	0.91	0.60
	60	0.11	0.52	0.90	0.65
5	30	0.12	0.57	0.88	0.63
	60	0.20	0.49	0.83	0.66
6	30	0.17	0.49	0.85	0.66
	60	0.21	0.51	0.82	0.66

the alternating irrigation (water logging- dry) in the second system, they found that the content of the crystalline iron oxides Fe<sub>d</sub> under the first system began to decrease gradually with the increase of the flooding period. While the results of Table 3 showed that the values of Fe<sub>d</sub> crystalline iron oxides in the dry soils ranged between

4.54 and 6.61 g Fe<sub>2</sub>O<sub>3</sub> kg<sup>-1</sup> soil, and the results also showed that the values of crystalline iron oxides fluctuated during the rice-growing season in that soil. It started with a gradual increase from the first month of taking the samples to reach its maximum during the third and fourth months, then the decrease resumed until the end of the planting season. This fluctuation in the values of crystalline iron oxides within dry soils is mainly due to the effect of the irrigation system applied in these soils, in which the water logging and drought conditions are successive, which are reflected in their effect in the cases of oxidation and reduction that encourage increasing in the accumulation and crystallization of iron oxides (Essa, 1990). While the change in the applied irrigation pattern and turning it into a continuous water logging after the fourth month of the cultivation season, which in turn reduced the Eh values in that soil, this was followed by the occurrence of a continued reduction case that inhibited the crystallization process of free iron oxides in that soil. (Wahid and Kamala, 1992) observed that the stability degree of both crystalline and amorphous iron oxides will change when the soil is exposed to a water logging condition, and it will all go toward the reduction case



**Fig. 5:** Distribution of total free iron oxides content in dry and waterlogged soils for the two depths 30 cm (a) and 60 cm (b)



**Fig. 6:** Distribution of crystalline free iron oxides content in dry and waterlogged soils for the two depths 30 cm (a) and 60 cm (b)

when the water logging process continues.

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