

## Effect of Applied Iron on Iron Desorption in Soil and Uptake by Wheat Plants

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### Abstract

Kinetic, fractionation and uptake studies were conducted in pot experiment to evaluate iron release and its bioavailability and uptake by wheat crop grown in calcareous soils. Iron applied in the form of Fe-EDDHA at rates of 0, 10, and 20 ppm Fe, in soils varying in contents of CaCO<sub>3</sub> (2.13, 14.66 and 25.34 %) at 20, 40 and 80 days. Results from the kinetic study proved that, the Elovich, power function, hyperbola and parabolic diffusion kinetic models gave high conformity to describe the desorption rate of iron from the studied soils. However, according to higher R<sup>2</sup> and lower SE values, both the Elovich and hyperbola models were the most appropriate models as compared to other kinetic models tested. Fractionation study indicated that, a gradual increase in different iron fractions was observed due to Fe application up to 40 days of incubation period. The effect of varying levels of Fe-EDDHA was significant; with respect to water soluble, exchangeable and Pb-displaceable iron content in soil. However, increasing CaCO<sub>3</sub> content in soils significantly decreased all iron fractions in the soils used. The effects of applied Fe resulted in significant differences regarding dry weight, available Fe, Ferrous iron and Fe uptake by wheat plants in pot experiment. Application of 20 ppm Fe recorded the highest as compared to other treatments. Regression equation proved that, wheat dry weight is mostly affected by both DTPA-Fe, Fe uptake by plant; water soluble Fe and exchangeable Fe in soil.

**Key words:** Fe-EDDHA, CaCO<sub>3</sub>, Ferrous Fe, water-soluble Fe, kinetics models, wheat plants.

### INTRODUCTION

Calcareous soils are common in arid and semi-arid climates and occur as inclusions in more humid regions, affecting over 1.5 billion acres of soil world-wide and comprising more than 25% of the soils in Egypt concentrated in north western region. The flux of Fe in calcareous soil can be investigated by means of kinetic experiments designed to measure the nature, the capacity and the rate of Fe release from soil. The difficulty of studying the kinetics of reaction in soils is largely due to its complexity. The mixture of inorganic and organic components of soil interacts and displays different types of sites with various reactivities for inorganic and organic adsorbents. The type of soil can drastically affect the reaction rate. However, metal sorption reactions on oxides and humic substance depend on the type of surface and the metal but the reaction rate appears to be rapid [1]. Most of Fe in soil is in the ferric form but dicots and monocots (Strategy I), except the Poaceae (Strategy II, [2], take up Fe<sup>+2</sup> and therefore have to reduce Fe<sup>+3</sup> before uptake. Iron uptake in Fe-deficient plants followed Michaelis-Menten kinetics up to about 30 μM and was linear at higher concentrations, indicating two kinetically distinct components in the uptake of Fe-phytosiderophores [3]. In the plant Fe is oxidized to Fe<sup>+3</sup> and transported mainly as citrate or malate, and most of the Fe in the plant is in the Fe<sup>+3</sup> forms [4]. Current interest in modeling the factors, which affect the biomass production, has created the need to quantify the flux of soil Fe between soil matrix and soil solution.

Sequential fractionation techniques are being used increasingly to provide more useful assessments of soil nutrients whether macro and micronutrients such as iron. The

concentrations of soluble and exchangeable Fe in calcareous soils are much lower than those necessary for adequate plant growth and plants have developed several mechanisms to make also other forms of Fe available [5]. The information on the contribution of each fraction to the total iron contents and their relationship with soil properties is meager especially in calcareous soil. The percentage contribution of soil iron fractions to total iron were studied by [6] and it was in following order: Residual iron > amorphous Fe-oxide occluded iron > organically bound iron > Mn-oxide occluded iron > Pb-displaceable iron > exchangeable iron > acid soluble > water soluble iron. The amount of iron in labile pools was very low and this could be the reason for the frequent appearance of iron chlorosis in calcareous Vertisols of Karnataka.

The majority of plants are able to grow and complete successfully on calcareous soils. However, an appreciable minority of species, the so called calcifuges, are unable to grow in such conditions because of limitations in their mineral nutrition. Often the primary limitation for these species is an inability to render the indigenous forms of soil micronutrients available for uptake, but there are also species that are limited by a deficiency of these nutrients like wheat [7]. Iron deficiency chlorosis is one of the major problems affecting a variety of crop species grown in calcareous soils. In severe cases iron deficiency chlorosis leads to failure of whole crop stands which in cropping systems with perennial plants results in high economical losses [8]. Moreover, in calcareous soils in which Fe deficiencies in plants are widespread, high soil pH decreases the solubility of this metal to very low levels, mainly because of the formation of inorganic Fe complexes [9]. Since the metal possesses a relatively high affinity for organic

chelators applied in light texture soils, the presence of synthetic or naturally occurring chelators can enhance considerably the metal concentrations in the soil solution [10]. The effects of micronutrients on wheat production in calcareous soils studied by [11]. The results showed that Fe fertilization by 20 kg ha<sup>-1</sup> Fe-EDDHA caused significant increase in grain yield, straw yield, 1000 grain weight, and the number of seeds per spikelet. With the application of iron, its concentration and total uptake in grain and flag leaves and the grain protein content increased significantly.

The main objectives of this work were to investigate the effect of the residence time and rate of Fe addition to soil system on iron desorption, iron fractions in soil and plants for maintaining a better strategy in Fe treatments in calcareous soils.

## MATERIALS AND METHODS

### Soils

Three soils, representing a wide range in physicochemical properties of some governorates of Egypt, i.e., Giza {Experimental farm, Cairo university, *Typic torrifluvents* (S<sub>1</sub>), Boheirah {Janakils, *Typic haplucaloids*, (S<sub>2</sub>)} and Alexandria Borg El-Arab North, *Typic haplucaloids*, (S<sub>3</sub>), were sampled from 0 to 15 cm in depth, and mixed. The soil samples were air dried and ground to pass through a 2 mm sieve for different physicochemical analysis and greenhouse experiments. Particle size distribution was determined by the pipette method, soil pH and EC were determined using soil: water suspension. Organic carbon was determined by dichromate oxidation, total calcium carbonate was determined by titration with acid, active CaCO<sub>3</sub> of the soils were determined by the 0.1M Ammonium oxalate, pH 8.3 method and available iron determined by atomic absorption after DTPA extraction. Some physical and chemical properties of these soils determined after [12] and are presented in Table (1). These soils used for conducting a pot experiment without cultivation (Kinetic and fractionation) and with wheat cultivation (uptake study) under the same condition and same time of sample collection.

**Table 1.** Some physical and chemical properties of the studied soil samples

Soil No.	pH (1:2.5)	EC (dS.m <sup>-1</sup> ) (1:5)	OM (%)	Total CaCO <sub>3</sub> (%)	Active CaCO <sub>3</sub> (%)	Clay (%)	DTPA-Fe (ppm)
S <sub>1</sub>	8.17	0.36	2.00	2.13	0.51	35.5	4.18
S <sub>2</sub>	8.30	0.24	0.55	14.66	8.25	20.12	3.05
S <sub>3</sub>	8.00	0.25	0.41	25.34	11.47	14.50	2.31

### Kinetic study

In the abovementioned soil samples varying in CaCO<sub>3</sub> at 2.13, 14.66 and 25.34 % CaCO<sub>3</sub> named as S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>, respectively, iron applied as Fe-EDDHA at 0, 10 and 20 ppm Fe named as Fe<sub>0</sub>, Fe<sub>1</sub> and Fe<sub>2</sub> and incubated for 20, 40 and 80 days without cultivation. Kinetics of Fe release from different treatments at different incubation times was carried out using

Electrical Stirred Flow unit method after [13]. Exactly 20 g of each Fe treated soils were put in the kinetic part of the device with 100 ml of 0.1N DTPA solutions. The system was vigorously shaken and the solution samples were received after different periods ranged between 1 min to 336 hrs at 25 ±2 °C and analyzed for their concentrations of Fe using atomic absorption. The Fe-release data were fitted to different empirical and theoretical models to select the best ones describing the kinetic data.

### Model used

In order to investigate the mechanism of desorption and potential rate-controlling steps such as mass transport and chemical reaction processes, several kinetic models were tested including the fractional power equation, the Elovich equation, a pseudo-first order equation and a hyperbola equation. The mathematical expressions are as follow:

#### Fractional power model

The fractional power function model is a modified form of the Freundlich equation and may be expressed by equation (1) [14] or its linear form as given in equation (2):

$$qt = at^b \quad (1)$$

$$\log q_t = \log a + b \log t \quad (2)$$

Where qt is the amount of Iron desorbed from soils at a time t, while a and b are constants with b < 1. The function a b is also a constant, being the specific sorption rate at unit time, i.e. when t = 1.

#### Elovich model

The Elovich or Roginsky-Zeldovich equation is generally expressed as follows [15]:

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (3)$$

Where q<sub>t</sub> is the amount of iron desorbed at a time t, a is the initial iron desorption rate [mg/ (g min)] and b is the desorption constant (g/mmol) during any one experiment. To simplify the Elovich equation, [16] assumed abt >> 1, and on applying the boundary conditions q<sub>t</sub> = 0 at t = 0 and q<sub>t</sub> = qt at t = t, equation (3) then becomes [1]  $qt = \beta \ln(\alpha b) + \beta \ln t \quad (4)$

Thus the constants can be obtained from the slope and intercept of the linear plot of qt versus ln t. Equation (4) will be used to test the applicability of the Elovich equation to the kinetics of Iron desorption from the studied soil samples.

Hyperbola model	Nonlinear eq. $y=x/(k*t+b)$	Linearized eq. $1/y=k-t/x$	Constraints $x \gg 0 \quad y \ll 0$
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**Pseudo-first order model**

For a batch contact time process where the rate of sorption of iron (II) on to the soil surface is proportional to the amount of iron (II) sorbed from the solution phase, the first-order kinetic equation may be expressed as:

$$dq_t / dt = k_1(q_e - q_t) \quad (5)$$

Where  $q_e$  and  $q_t$  are desorption capacity (ug/g) of the Iron at equilibrium and at a time  $t$ , respectively, and  $k_1$  is the rate constant for pseudo-first order desorption (l/min). After integration and applying boundary conditions, viz. that the initial conditions are  $(q_e - q_t) = 0$  at  $t = 0$ , equation (5) becomes:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

The equation, applicable to experimental results, generally differs from a true first-order equation in two ways [14]: (i) the parameter  $k_1(q_e - q_t)$  does not represent the number of available sites; and (ii) the parameter  $\ln q_e$  is an adjustable parameter which is often not equal to the intercept of a plot of  $\ln (q_e - q_t)$  versus  $t$ , whereas for a true first-order process  $\ln q_e$  should be equal to the intercept of a plot of  $\ln(q_e - q_t)$  versus  $t$ .

In this study we also fitted the kinetic data obtained according to the following model:

The kinetic parameters in the tested equations were calculated for the three soils under different treatments, compared and discussed. The regression analysis to test the conformity of Fe release to the applied models and testing for significant differences in rate coefficients and cumulative quantity of Fe desorbed was done using regression SAS software [17].

**Iron fractionation**

In the same soil samples used for kinetic study, iron fractions content of soils were sequentially extracted at 20, 40 and 80 days of incubation as described by Miller *et al.* [18]. The reagents employed and chemical forms solubilized with 0.5-g sample weights are listed as follows: Soluble: 20-ml H<sub>2</sub>O, shaken for 16 hrs, Exchangeable: 20-ml 0.5 M Ca (NO<sub>3</sub>)<sub>2</sub>, shaken 16 hrs, Pb-displaceable: 20-ml 0.5 M Pb(NO<sub>3</sub>)<sub>2</sub> + 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub>, shaken 16 hrs, Acid soluble: 20-ml 0.44 M CH<sub>3</sub>COOH + 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub> shaken 8 hrs, Manganese oxide-occluded: 20 ml 0.01 M NH<sub>2</sub>OH.HCl + 0.1 M HNO<sub>3</sub> shaken 30 min, Organically bound: 20-ml 0.1 M K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, shaken 24 hrs and Amorphous Fe oxide-occluded: 20-ml 0.175M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.1M H<sub>2</sub>C<sub>2</sub>O<sub>7</sub>, shaken 4hrs in darkness. After each successive extraction, centrifuging for 30 min did separation. The supernatants were removed with a pipette, filtered and analyzed for iron Atomic Absorption Spectrophotometer (Shimadzu, AA 630-11).

**Iron uptake by wheat plants**

The pot experiment was conducted at National Research Center, Egypt to understand the effect of applied iron on Fe availability and uptake by wheat plants grown in same soils used for kinetic and fractionation study (without cultivation) and treated with same iron treatments. Pots were filled with ten Kg of air-dry calcareous soil at 2.13, 14.66 and 25.34 % CaCO<sub>3</sub> named as S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>, respectively. Wheat (*cv.* Sakha 8) was germinated and ten uniform seedlings planted in each pot and irrigated to field capacity. All pots were weighed daily and the water loss was replenished with tap water. Pot experiment of wheat plant and incubation (without plant used for kinetic and

fractionation studies) were performed under the same times and conditions. The experimental treatments replicated three times in a complete randomly design. Plant samples were taken at 20, 40 and 80 day after sowing, Fe<sup>2+</sup> iron estimated in the fresh leaves. Ferrous iron analyzed by the methods reported by [19]. Available iron was determined as described by [20]. All obtained data were subjected to statistical analysis according to SAS program [17].

**RESULTS**

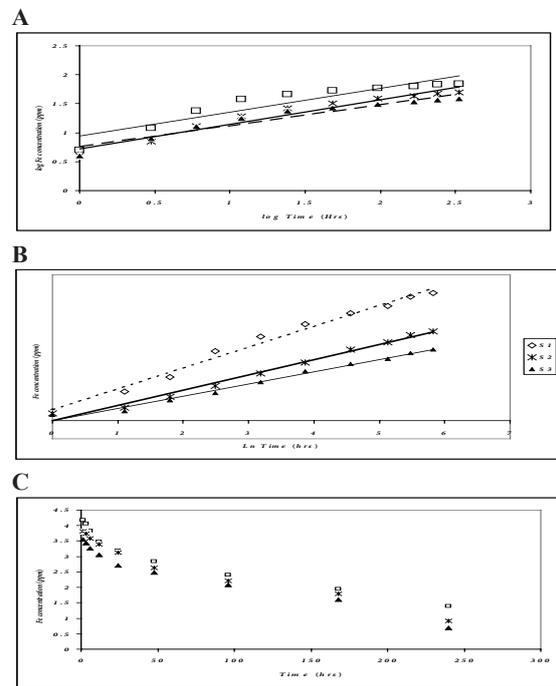
**Fitting of kinetic data to used models**

**Fractional power model**

Fig. 1A shows a plot of log q<sub>t</sub> against log t of the fractional power function equation for the results of iron desorption from the studied soil samples at higher ion concentration and 80 days of incubation time. The figure shows that, although a linear relationship existed over the initial 15-min period of the desorption process; the overall line was not straight.

**Elovich model**

Fig. 1B shows a plot of log q<sub>t</sub> against log t of the fractional power function equation for the results of Fe desorption from different studied soils at higher ion concentrations. The figure shows that, again the linear relationship existed overall the entire period of the desorption process in S<sub>2</sub> and S<sub>3</sub>, however, the overall line was not straight in the 1<sup>st</sup> used soil sample.



**Figure 1.** Plot of fractional power function equation (A), Elovich (B) and 1<sup>st</sup> order (C) for Fe desorption from the studied soil samples at higher initial concentration rate applied

**Pseudo-first order model**

The results of desorption of iron from used soils have been represented in the form of the first order equation in **Fig. 1C** at higher initial ion concentrations applied and 80 days of incubation. From these plot, a linear relationship between  $\ln (q_e - qt)$  and  $t$  was established for the later portion (15 min to 336 hrs) with high correlation coefficients ( $> 0.987$ ). These plots showed different distinct linear regions within individual sets of data. In these cases, it was thus necessary to perform multiple regressions on different ranges of the data. The kinetics could be approximated by two basic equations, each valid over a limited range of time: the fractional power equation at the beginning of the experiment (50 min) and the first-order equation when saturation was approached (50 min – 336 hrs). However, the Elovich equation provides an excellent description of desorption of iron from used soils (**Figures 1 B**) with high correlation coefficients. So, the experimental results could be described by the Elovich model.

**Hyperbola model**

The hyperbola kinetic model in the form:  $Y=x / (k*t + b)$  gave high fitting to kinetic data (**Fig. 2**). Results indicated that under our experimental conditions, the model showed high conformity represented by higher  $r^2$  compared with other used models.

**Comparison between rate constants in Elovich and Hyperbola**

Data in **Table 2** represent rate constants  $\alpha$  and  $\beta$  of Elovich kinetic model, coefficients of determination  $R^2$  and standard errors SE of Fe desorption from the studied soil samples treated with tow rates of Fe beside control and collected at 20, 40 and **Table 2**. Calculated values of  $\beta$  and  $\alpha$  of the Elovich Equation for Fe desorption from used soils as affected by  $CaCO_3$  content and time of incubation.

Soils (S)	Fe added (ppm)	20 days		40 days		80 days	
		B	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$
S1	Fe <sub>0</sub>	11.93	1.24	6.83	1.39	4.13	0.51
	Fe1	14.39	4.42	9.32	4.77	7.53	3.75
	Fe2	16.34	17.09	13.18	10.96	11.73	4.63
S2	Fe <sub>0</sub>	7.92	1.95	4.91	0.1	2.91	0.23
	Fe1	10.41	2.73	6.94	0.29	5.29	0.38
	Fe2	12.23	6.15	10.7	2.15	8.38	0.4
S3	Fe <sub>0</sub>	6.82	0.26	3.66	0.63	2.51	0.09
	Fe1	8.41	0.29	4.84	2.69	4.21	1.34
	Fe2	9.93	2.21	7.24	2.92	6.22	2.72

S<sub>1</sub>: 2.13% CaCO<sub>3</sub>, S<sub>2</sub>: 14.66 % CaCO<sub>3</sub>, S<sub>3</sub>: .25.34% CaCO<sub>3</sub> and Fe<sub>0</sub>: -Fe, Fe<sub>1</sub>: 10 ppm Fe, Fe<sub>2</sub>: 20 ppm Fe as Fe-EDDHA.

80 days. Both equations showed higher conformity in describing the kinetic data by higher  $R^2$  ranged between 0.96\*\*\* to 0.99\*\*\* beside lower SE compared with other used models.

It should be mentioned here that correlation analysis between Fe uptake and the rate constants of different models applied showed high and significant correlation ranged between 0.88\*\* and 0.99\*\* in different used soils and under both rates of Fe applied in this study and times of incubation. For example, data showed that after 20 days, correlation values between Fe uptake by wheat and  $\beta$  rate constant of Elovich equation were 0.998\*\*, 0.997 and 0.98 in S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>. After 40 days, the correlation values were 0.893\*\*, 0.889\*\* and 0.901\*\*. The respective values were 0.893\*\*, 0.934\*\* and 0.918\*\*. The  $\beta$  constant showed high significant once in relation to plant uptake by different authors [13] and [21].

Data in **Table 3** showed that increasing the application rate of Fe in different soils and under different sampling times, increased the intensity factor represented by  $k$  constant. Concerning the combined effect of incubation time and the presence of CaCO<sub>3</sub> in used soils on the intensity factor, it should be mentioned here that both factors drastically reduced  $k$  constant to about 82 % in S<sub>3</sub> after 80 day of sowing compared with S<sub>1</sub> at high rate of added Fe.

**Table 3.** Calculated Values of  $k$  and  $b$  of the Hyperbola equation for Fe desorption from used soils as affected by CaCO<sub>3</sub> content and time of incubation.

Soils (S)	Fe added (ppm)	20 days		40 days		80 days	
		K	b	k	b	k	b
S1	Fe <sub>0</sub>	5.3	19.1	2.0	19.0	1.1	18.2
	Fe1	8.9	13.9	5.6	18.5	3.2	16.2
	Fe2	9.5	10.6	8.7	15.4	5.3	14.7
S2	Fe <sub>0</sub>	3.2	20.9	1.0	3.80	1.1	0.06
	Fe1	6.7	20.7	3.3	3.01	2.2	0.04
	Fe2	9.1	15.9	6.7	2.06	4.3	0.03
S3	Fe <sub>0</sub>	1.0	0.02	1.0	0.06	1.1	0.09
	Fe1	3.2	0.02	3.3	0.04	3.5	0.05
	Fe2	5.6	0.02	4.4	0.03	3.6	0.03

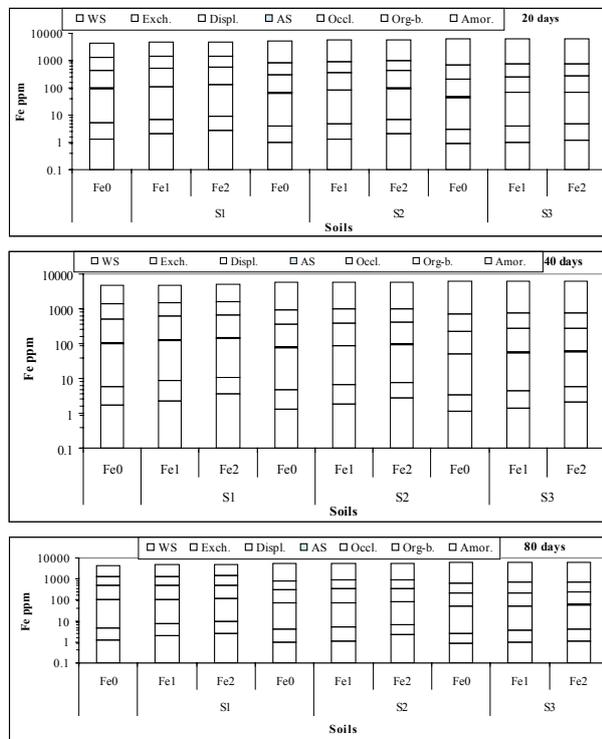
S<sub>1</sub>: 2.13% CaCO<sub>3</sub>, S<sub>2</sub>: 14.66 % CaCO<sub>3</sub>, S<sub>3</sub>: .25.34% CaCO<sub>3</sub> and Fe<sub>0</sub>: -Fe, Fe<sub>1</sub>: 10 ppm Fe, Fe<sub>2</sub>: 20 ppm Fe as Fe-EDDHA.

As to the capacity factor represented by  $b$  constant, the effect of abovementioned factors especially active CaCO<sub>3</sub> was more pronounced. Data showed that after 80 days of incubation, the  $b$  was decreased from 14.7 to 0.03 in S<sub>1</sub> and S<sub>3</sub> respectively. The same trend was also observed in 20 and 40 days.

**Fractionation of soil iron**

Recently, attempts have been made to assess the bioavailability of metals in soils and sediments using sequential extraction [18]. Such assessments assume that metal bioavailability decreased with each successive extraction step in the procedure. Therefore, metals in water soluble and exchangeable fractions would be readily bio-available to growing plants, whereas the metal in the residual is tightly bound and would not expected to be released under natural conditions [22]. Data of the sequential extraction procedure indicated that

concerning the time of incubation, as the time period increased a gradual significant increasing in all forms of iron content of used soils was pronounced. This phenomenon was noticed up to 40 days of incubation and thereafter decreased till 80 days. In relation to the effect of CaCO<sub>3</sub> content in used soils (Fig. 3). Data indicated that the significant depressing effect of CaCO<sub>3</sub> levels in soil on the availability of iron could be due to oxidation of soluble native iron through direct reaction with CaCO<sub>3</sub> and the increased soil pH due to hydrolysis of CaCO<sub>3</sub>. When iron was added to these soils, all the forms of iron increased with respect to the dose applied, which was probably due to slow oxidation of soluble iron into various insoluble higher oxidation states. The effect of applied iron was only significant with water soluble, exchangeable and Pb-displaceable iron contents in soil. However, an increase in CaCO<sub>3</sub> levels in soil significantly decreased all iron fractions in soil at varying days after sowing period.



**WS:** water soluble Fe, **Exch:** Exchangeable Fe, **Displ:** Pb displaceable Fe, **AS:** Acid soluble Fe, **Occl.** Mn oxide occluded Fe, **Org-b:** Organically bound Fe and **Amor:** Amorphous Fe.

**Figure 3.** Effect of CaCO<sub>3</sub> and iron application on different Fe fractions (ppm) in soil at different day of incubation.

**Response of wheat to iron application**

**Dry matter of wheat**

The results from pot experiment in Table 4 indicate that iron application had significant influence on dry weight during the growth period of wheat plants grown in soil varying in calcium carbonate contents. At 80 days, application of 20 ppm Fe as Fe-EDDHA registered the highest dry weight (45.5 g pot<sup>-1</sup>) and it was significantly superior over 10 ppm Fe (40.8 g pot<sup>-1</sup>) in the soil at 2.13 % CaCO<sub>3</sub>. The lowest total dry weight obtained in

the treatment receiving no iron (control) at the highest CaCO<sub>3</sub> content. The interaction effects were not significant at different stages of wheat crop.

**Ferrous iron content of wheat**

Iron application to soil distinctly increased ferrous iron **Table 4.** Effect of CaCO<sub>3</sub> and Fe application on dry weight and ferrous Fe at different days of wheat sowing.

Soils (S)	Applied Fe (ppm)	Dry weight (g pot <sup>-1</sup> )			Ferrous Fe (ppm) in plants		
		20 day	40 day	80 day	20 day	40 day	80 day
S <sub>1</sub>	Fe <sub>0</sub>	4.5	13.1	36.1	21.3	17.6	11.4
	Fe <sub>1</sub>	5.6	15.6	40.8	38.2	51.7	43.5
	Fe <sub>2</sub>	6.8	17.0	45.5	46.3	59.1	48.2
S <sub>2</sub>	Fe <sub>0</sub>	4.0	10.7	33.6	18.7	15.0	10.7
	Fe <sub>1</sub>	4.7	11.6	36.0	31.2	38.3	21.4
	Fe <sub>2</sub>	5.1	13.4	40.8	40.8	43.7	25.0
S <sub>3</sub>	Fe <sub>0</sub>	3.8	9.8	31.3	13.4	12.7	8.70
	Fe <sub>1</sub>	4.2	10.5	33.6	21.5	24.3	15.8
	Fe <sub>2</sub>	4.7	10.7	35.1	22.3	25.6	17.0
<b>LSD (1%)</b>	S	0.51	0.95	2.81	1.11	1.73	1.40
	Fe	0.51	0.95	2.81	1.11	1.73	1.40
	S x Fe	NS	NS	NS	1.93	3.00	2.41

S<sub>1</sub>: 2.13% CaCO<sub>3</sub>, S<sub>2</sub>: 14.66 % CaCO<sub>3</sub>, S<sub>3</sub>: .25.34% CaCO<sub>3</sub> and Fe<sub>0</sub>: -Fe, Fe<sub>1</sub>: 10 ppm Fe, Fe<sub>2</sub>: 20 ppm Fe as Fe-EDDHA

content of wheat plants at different CaCO<sub>3</sub> levels in soils (Table 4). The pots receiving Fe<sub>2</sub> increased ferrous iron by (235.8 and 59.6 %) over the Fe<sub>0</sub> treatment in the soil having 2.13 % CaCO<sub>3</sub> at 40 and 80 days, respectively. This could be due to increased iron availability in soil and the direct uptake of ferrous iron by leaves resulting in higher production of chlorophyll, dry matter and higher total iron content of plants. Similar results recorded [23] in groundnut. The lowest values of Ferrous Fe content were recorded at the highest CaCO<sub>3</sub> levels in soil with no iron applied at 80 days of wheat sowing.

**DTPA-Fe in soils**

**Table 5.** Effect of calcareousness and iron application on DTPA-Fe in soil and Fe uptake at different days of wheat sowing.

Soils (S)	Applied Fe (ppm)	DTPA-Fe (ppm) in soil			Fe uptake (mg pot <sup>-1</sup> ) by plant		
		20 day	40 day	80 day	20 day	40 day	80 day
S <sub>1</sub>	Fe <sub>0</sub>	4.41	4.31	4.17	1.82	4.07	12.30
	Fe <sub>1</sub>	6.12	5.63	5.21	2.42	5.26	14.97
	Fe <sub>2</sub>	6.38	6.11	5.41	2.91	6.54	17.88
S <sub>2</sub>	Fe <sub>0</sub>	3.29	3.17	3.02	1.26	3.87	11.75
	Fe <sub>1</sub>	4.93	4.56	4.11	1.75	5.03	13.48
	Fe <sub>2</sub>	5.12	5.07	4.76	1.97	5.23	15.65
S <sub>3</sub>	Fe <sub>0</sub>	2.61	2.31	2.27	1.06	3.37	11.36
	Fe <sub>1</sub>	3.34	3.18	2.65	1.66	4.38	13.11
	Fe <sub>2</sub>	3.94	3.77	3.28	1.73	4.96	14.89
<b>LSD (1%)</b>	S	1.18	1.06	0.52	0.13	NS	0.50
	Fe	1.18	1.06	0.52	0.13	1.08	0.50
	S x Fe	NS	NS	NS	NS	NS	0.86

S<sub>1</sub>: 2.13% CaCO<sub>3</sub>, S<sub>2</sub>: 14.66 % CaCO<sub>3</sub>, S<sub>3</sub>: .25.34% CaCO<sub>3</sub> and Fe<sub>0</sub>: -Fe, Fe<sub>1</sub>: 10 ppm Fe, Fe<sub>2</sub>: 20 ppm Fe as Fe-EDDHA.

The data on DTPA-extractable iron indicate that levels of applied iron significantly increased the DTPA-extractable iron

at different growth stages of wheat (Table 5). The treatment Fe<sub>2</sub> recorded the highest percent increase in DTPA-extractable iron (41.8 and 29.7 %) as compared to Fe<sub>1</sub> (7.1 and 24.9 %) over no Fe treatment (Fe<sub>0</sub>) at 40 and 80 days in soil having 2.13 % CaCO<sub>3</sub>. This could be due to more vegetative growth and root growth which release hydrogen ions, phenolic compounds and organic acids as well as phytosiderophorus helped in increased availability in soils. The lowest available iron obtained in the highest CaCO<sub>3</sub> in soils receiving no iron.

#### Iron uptake by wheat

Iron application significantly increased iron uptake by wheat in Table 5. The pots receiving Fe<sub>2</sub> treatment registered significantly higher iron uptake (1.91 and 17.88 mg pot<sup>-1</sup>) over the control treatments at 20 and 80 days in control soil (2.13 % CaCO<sub>3</sub>), respectively. The soil containing higher CaCO<sub>3</sub> levels (S<sub>3</sub>) recorded the lowest iron uptake (1.06, 3.37 and 11.36 mg pot<sup>-1</sup>) as compared to S<sub>1</sub> (1.82, 4.07 and 12.30 mg pot<sup>-1</sup>) at different growth periods over the iron uptake obtained in the control treatment, respectively.

#### Correlation analysis:

Table 6 illustrates the simple correlations between wheat dry weight and iron fractions in soil and plant. Data revealed that dry weight is highly correlated with DTPA-Fe, Fe uptake by plant, water soluble-Fe, exchangeable-Fe and displaceable-Fe in soil. Also, one can notice that there were significant correlations between DTPA-Fe in soil and ferrous iron in plant, while the relations were highly positive significant correlation with each of water soluble-Fe, exchangeable-Fe and displaceable-Fe in soil wheat dry weight (DW) and ferrous iron in plant. According to the ferrous iron in plant, significant positive correlations were observed with DTPA-Fe and displaceable-Fe in soil and negative correlation with iron uptake by wheat plants.

#### Regression analysis

Multi regression equations were estimated from obtained data to assess the close relations between dry weights as

Table 6. Simple correlation among some studied parameters

	Dray weight	Ferrous Fe	DTPA-Fe	Fe Uptake	Water soluble Fe	Exchangeable Fe
Ferrous Fe	-0.532**					
DTPA-Fe	0.343**	0.438*				
Fe uptake	0.647**	-0.244*	-0.026			
Water soluble Fe	0.600**	0.091	0.829**	0.055		
Exchangeable Fe	0.557**	0.200	0.922**	0.086	0.913**	
Displaceable Fe	0.403**	0.264*	0.912**	0.039	0.799**	0.924**

independent variable with ferrous iron in plant, DTPA-Fe, Fe uptake by plant; water soluble Fe in soil, exchangeable Fe in soil and displaceable Fe in soil as dependant variables. Equation as follows:

Dry weight = -4.605 - 0.699 Ferrous Fe in plant + 4.225 DTPA-Fe + 1.264 Fe uptake by plant + 4.291 water soluble Fe in soil + 4.945 Exchangeable Fe in soil - 0.227 Displaceable Fe in soil R<sup>2</sup> = 0.973\*\*

## DISCUSSION

In Kinetic study, the  $\beta$  values of Elovich equation in Table 2 significantly increases by increasing rate of Fe applied regardless soil type. For example, in S<sub>1</sub>, increasing the rate of Fe addition to 10 and 20 mg Fe kg<sup>-1</sup> soil, led to increase  $\beta$  constant by about 30 and 45% over control and the same trend was also observed in other soil. The  $\beta$  value in Elovich equation was shown by Elkhatib and Hern [24] to be inversely proportional to the soil supplying power of the studied ion to plant. Chien and Clayton [16] also showed that the decrease in  $\beta$  enhance the reaction rate. Sikora *et al.* [25] reported that  $\beta$  constant is an important parameter to define desorption rate  $di/dt$  throughout the whole dissolution period of added ion(s). The effect of time period on rate of Fe desorption from the three soil samples was also studied. Data shows that increasing the time of incubation, generally, led to decrease the rate of Fe desorption. In S<sub>1</sub>,  $\beta$  values decreased to 13.18 and 11.73 by increasing the time to 40 and 80 days in 10 and 20 mg Fe/kg soil, respectively. These decreasing values represent almost half and one third of the starting value 11.93 after 40 day incubation. The same trend was also observed in other used soils.

The effect of the presence of CaCO<sub>3</sub> in total or active form on Fe desorption are presented in the same Table. Beside the effect of time period in decreasing the rate of Fe release, data indicates that at any time of incubation increasing of active CaCO<sub>3</sub> in soil led to decrease in Fe desorption. At the beginning of the experiment at 10 mg Fe/kg rate,  $\beta$  values decreased 14.39 to 10.41 and 8.41 in S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> respectively, the same values were 7.53, 5.29 and 4.21 at 80 days time, these values represents more than 50 % decreasing in rate of Fe desorption. The same trend also observed at high rate of application. Concerning the  $\alpha$  constant which is suggested to be an important parameter in defining  $d[P]/d[t]$  at low time period [25], data shows that in each soil increasing rate of Fe applied led to increase this constant. In contrast by increasing the time period and increasing of active CaCO<sub>3</sub>, this constant recorded the lower values. The Hyperbola equation, which showed conformity to

describe the kinetic data almost, takes the same trend of Elovich equation. In this study we assume that the applied Fe in used soil samples undergoes three different mechanisms through adsorption reactions: inner-sphere complexes, outer-sphere complexes, and diffusion. Outer-sphere bonds consist of a solvated ion (Fe in our case) that forms a complex with charged clay mineral. The primary bonding force is electrostatic. An inner-sphere complex is partially dehydrated; the ion forms a direct ionic or covalent bond with the surface function groups. A diffusion ion exists in the water layers near the surface and

is held by electrostatic attraction from permanent charges that exist in the solid structure. However, it is possible that these different mechanisms may influence the rate of Fe desorption and subsequently the applied model (s) describing the rate process.

The sequential extraction of iron concluded that, as the time period increased a gradual significant increasing in all forms of iron content of used soils up to 40 days and thereafter decreased (Fig.3). The decrease in iron fractions after 40 days may be due to conversion of soluble form of iron into insoluble form through precipitation reactions of  $\text{FeCO}_3$  and  $\text{Fe}_3(\text{OH})_8$ . The results observed in this study are in accordance with that reported by Hellal [6] and Yerriswamy *et al.*[26]. The time of incubation under optimum moisture and temperature conditions has resulted in the decrease of iron extracted because some of the added soluble iron might have changed to such higher oxides and hydroxides

In pot experiment, DTPA-extractable iron significantly increases due to the levels of applied iron at different growth stages of wheat (Table 5). This could be due to more vegetative growth and root growth which release hydrogen ions, phenolic compounds and organic acids as well as phytosiderophorus helped in increased availability in soils. Similar observations were recorded by Marschner and Romheld [27]. The trend of higher uptake of iron in the treatments receiving 20 ppm iron as Fe-EDDHA could be due to increased iron availability in soil and the direct uptake of ferrous iron by leaves resulting in higher production of chlorophyll, dry matter and higher uptake of iron by wheat plants. Similar results were observed by Sarkar [28]. From the Regression analysis, the correlation of determination was highly significant (0.973\*\*). Also, one can notice that wheat dry weight is more affected by both DTPA-Fe, Fe uptake by plant; water soluble Fe in soil, exchangeable Fe in soil water. The opposite was true in case of ferrous iron in plant and displaceable Fe in soil. It may have some direct effect on iron availability in soil and its uptake by plants.

## CONCLUSION

Under experimental conditions, kinetic study evaluated the effect of rate of Fe applied and residence time on Fe desorption from some calcareous soil varied in their  $\text{CaCO}_3$  content. Elovich and Hyperbola models were the best fitted ones by high coefficients of determination  $R^2$  and lower SE compared with others. Application of Fe fertilizers increased the rate of Fe desorption from the used soils. Moreover, both the presence and increasing of  $\text{CaCO}_3$  percent in used soil and increasing of time of soil incubation, all led to decrease the rate of Fe desorbed. The fractionation of Fe in used soils indicated that  $\text{CaCO}_3$  content and residence time tested were the most factors influencing Fe distribution in such soils. Water soluble and exchangeable Fe proved their importance as components of available Fe in soil consequently Fe uptake by plants. Application of the higher rate of iron (20 ppm) as Fe EDDHA in the calcareous soil used was important for increasing the release rate, available and uptake of iron resulting in significant increase of growth and yield of wheat plants. This study could recommend that application of high rate of Fe in these soil types is necessary for correcting

the deficiency symptoms of Fe and increasing the yield of crop grown in such soils.

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