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Humic Acid Influence on Chemically Extractable forms of Iron and Manganese in some Calcareous Soils

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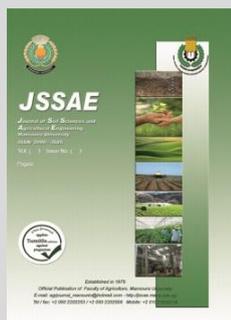
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ABSTRACT

In a split-split plot design with three replicates, a vitro kinetic experiment was carried out during two months to study the effect of both individual applications of either of two sources of humic acids (HAs) react with (or without) Fe or Mn on desorption of both micronutrients from three calcareous soils varying in their active CaCO_3 contents. Each HA was applied at a rate of 100 mg kg^{-1} soil. Each of Fe and Mn was added in the acetate form (CH_3COO) at a rate of 50 mg kg^{-1} soil. Results showed that the application of HAs with Fe or Mn led to minimizing fixation of both ions on soil particles compared to the control soil (untreated soil). A kinetic study implied used three different models well described the rate of Fe and Mn desorption from the treated soils by having a high and significant coefficient of determination R^2 and low standard error SE. According to the rate constants of the used models, applications of either the two HA with Fe or Mn were associated with a significant increase in the rate of both ions desorption with some prefer ability to HAP (derived from pudrite) compared to HAC (derived from clover straw compost). Different mechanisms take place between CaCO_3 soil particles, HAs and Fe or Mn systems were discussed.

Keywords: Humic acids, Iron, Manganese, calcareous soil.



INTRODUCTION

Calcareous soils are common in the arid areas of the earth (FAO, 2016) occupying $>30\%$ of the earth's surface, and their CaCO_3 content varies from just detectable up to 95% (Marschner, 1995). Calcareous soils spread over a wide area along the northern coast of Egypt beside of some scattered areas within El-Fayoum Governorate These soils may suffer from different problems such as the formation of a calcareous surface crust, formation of a hard pan at different depths of soil and relatively high pH value that adversely affects availability of the nutritive elements and consequently reduces land crop productivity.

Furthermore, cultivation of calcareous soils presents many challenges, such as low water holding capacity, high infiltration rate, poor structure, low organic matter (OM) and clay contents, low CEC, loss of nutrients via fixation, deep percolation, and cracking, , beside imbalance among fertilizers elements (El-Hady and Abo-Sedera, 2006; FAO, 2016). Fixation phenomenon of micronutrients represents the most important problem in such soils. Total content of CaCO_3 and the active CaCO_3 fractions with high specific surface area are major factors controlling this fixation (Morse et al. 2007). However, high pH is the major factor responsible for low bioavailability of plant nutrients in calcareous soils. These soils more have pH values in the range of 7.6 to 8.3 (Thomas et al. 2012).

Iron deficiency is a major problem in calcareous soils due to its low solubility and bioavailability because of their high pH values and bicarbonate content of lime

(Hooda, 2010). The World Health Organization (WHO, 2010) documented that about 25% of the world's population suffers from anemia resulted from Fe deficiency.

Manganese is an essential micronutrient for all organisms, playing an important role in tissue and bone formation, in reproductive functions, and carbohydrate and lipid metabolisms and is an important cofactor in numerous enzymes (Dos Anjos *et al.*, 2007). In turn, a deficiency of manganese is most often found in soils that are saline and alkaline, calcareous, or peaty (McBride, 1994)

Soils known to cause Mn deficiency in susceptible crops are usually impoverished siliceous and calcareous sandy soils of neutral or alkaline pH that favor chemical and microbial oxidation and immobilization of plant-available Mn^{2+} . This Mn deficiency occurs in soils, even if these soils contain large reserves of total Mn relative to the amounts removed in crop harvests (Rengel, 2015).

Humic substances (HS) are macromolecular complex mixtures comprised of an aromatic hydroxycarboxylic acid and play a vital role in the mobility and fate of plant nutrients (Yang *et al.*, 2013). It is well known that humic substances improve the chemical, biological and physical properties of calcareous soils which, in turn, influence the production capacity (Nardi *et al.*, 2002). Humic acids (HAs) and fulvic acids (FAs) are two major fractions of humic substance that influence plant growth via improving the physical properties, fertility and moisture condition of the soil (Chassapis *et al.*, 2009).

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The objectives of this study are: (1) to give an ideas about Fe and Mn reaction in calcareous soils through the kinetic approach (2) to evaluate the different techniques of humic acids application to calcareous soils to minimize Fe and Mn fixation in calcareous soils through the theoretical and empirical kinetic models (3) to find out the best type of HA that should be applied in calcareous soils to increase manganese and Fe release from these soils.

MATERIALS AND METHODS

Soils

The surface calcareous (*Typic calcids*) soil samples (0-30 cm) used in this study were collected from three different locations of Maryout Station in West El Delta-Egypt . The collected soil samples were air-dried and screened through a 2-mm sieve. Some physical and chemical properties of the investigated soils are presented in Table (1).

Table 1. Some physical and chemical characteristics of the studied soils.

Soil No.	Particle size distribution (%)			Textural class	pH in1: 2.5 soil –water suspension	Soil property					Available nutrients (mgkg ⁻¹ soil)	
	Total sand	Silt	Clay			Total CaCO ₃ (%)	Active CaCO ₃ %	Organic matter (%)	EC (dSm ⁻¹ ,soil paste extract)	Surface area m ² g ⁻¹	Fe	Mn
1	24	40	36	clay loam	7.2	24.64	17.90	0.68	5.58	170	5.98	2.9
2	34	35	31	Clay loam	7.4	19.98	9.30	0.57	5.42	155	5.83	2.9
3	44	44	12	loam	7.8	14.87	4.58	0.31	5.25	62	3.85	2.2

Experimental work

An incubation experiment was conducted at the laboratory of Physics and Chemistry Department, Desert Research Center, Egypt to study the effect of application of either Fe or Mn solely or in combination with humic acid prepared from pudrite (HAP) or extracted from clover compost (HAC) on kinetic of Fe and Mn in three calcareous soils differing in their Ca CO₃ content. The prepared humic acids were fractionated and purified according to the methods described by Baglieri et al. (2007) ,Susilawati et al. (2008) and Huculak –Mczka et al. (2018) .The most important characteristics of the used humic acids are presented in Table (2).

In selected soil samples, a 200g each were treated by the follow:

A: Sole application of either Fe or Mn at a rate of 50 mg kg⁻¹ to soils without humic acid

B: Application of HAP at a rate of 100 mg kg⁻¹ followed by application of the aforementioned concentration of either Fe or Mn

C: Sole application of either Fe or Mn at the aforementioned concentration to soils followed by HAP at a rate of 100 mg kg⁻¹soil.

D Application of either Fe or Mn together with HAP at their aforementioned concentrations

The aforementioned treatments were repeated once again but after replacing HAP by HAC.

All additives were mixed thoroughly with the concerned soils and left for incubation for 120-day period at lab temperature. Each of the aforementioned treatments was repeated three times, thereafter, the incubated soils were air dried, crushed and sieved through a 2 mm sieve.

Table 2. Chemical analysis of the studied humic acids

Humic acid	Source	C %	H%	Fe (mgkg ⁻¹)	C/N	C/P	N %	pH
HAP	From pudrite	45.18	5.50	335	48.06	65.5	0.94	6.35
HAC	From compost of clover straw	43.85	5.28	421	35.08	69.8	1.25	6.42

Kinetics study

After two months of incubation, five grams portion of each previously incubated soil was shaken with a 25 ml volume of DTPA(Lindsay and Norvell 1978) on an end-over-end circulatory shaker for 1, 5, 10, 30, 60, 120, and 1440 min at 25±2 °C, centrifuged at 2500 rpm (≈1000g) and the supernatant was taken for analysis of Fe and Mn using Inductively Coupled Argon Plasma, iCAP 6500 Duo (Thermo Scientific, England)..

An array of kinetic models including represented by Modified Freundlich, Elovich, parabolic Diffusion have been employed to examine the kinetics of iron and manganese release. The higher the coefficient of determination R² and the lower the SE values, the best fitting equation(s) could be used to describe the kinetic phenomenon. The mathematical expressions of these models are presented in Table 3.

Table 3. Different kinetic models used to describe the kinetic data.

Model	Integrated Form	Reference
Modified Freundlich equation	Log qt = log b + a log t	
Elovich	Q=a ln ba + a ln t	Sparks 1988
Parabolic Diffusion	Q=b + at ^{0.5}	

Where: qt is the amount of Fe or Mn desorbed (mg/kg) at time t, a and b are constants

Statistical analysis

In this experiment, the regression analysis was carried out in order to determine the conformity of iron and

manganese release to specific equation(s). Statistical analysis was performed using the SPSS 19.0 software and Microsoft Excel 2010 packages.

RESULTS AND DISCUSSION

Kinetics of Fe release from the calcareous soils as affected by time of humic acids application

Results depicted in Figure (1) show that application of iron (Fe^{2+}) applied individually (A treatment) to all the studied calcareous soils gave the lowest values of Fe desorption from the studied soils through the entire reaction time (1440 min). Numerically, the range of Fe^{2+} desorption ranged between 2.1 and 2.3 $mg\ kg^{-1}$ soil. Sorption reactions on the soil-water interface take a part in controlling the ion availability in soil (Thompson and Goynes, 2012). Carbonate increases Fe sorption in soils (Taalab *et al.*, 2019). Therefore, both the sorption reaction and the carbonate content of the studied calcareous might take a part in limiting release of Fe from these soils.

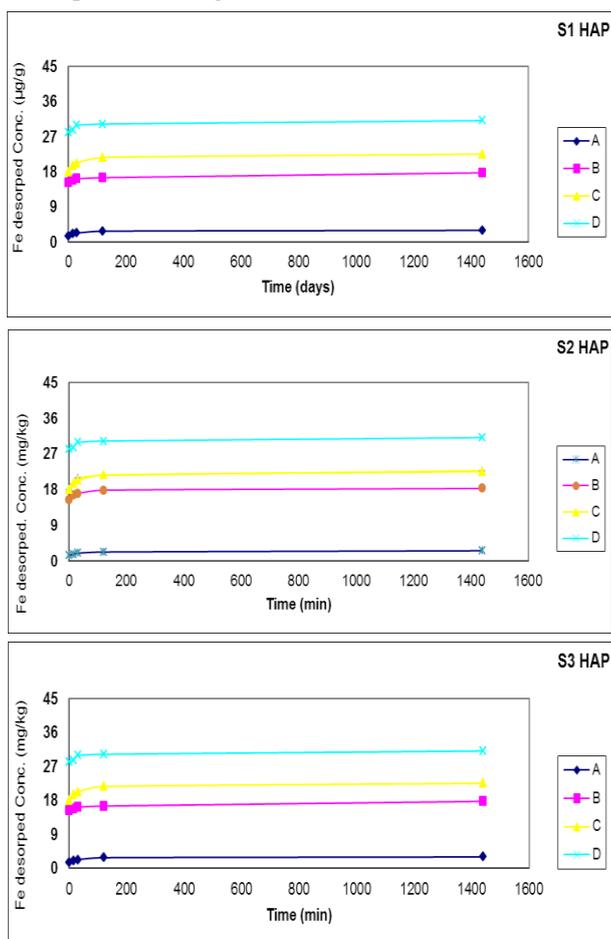


Figure 1. Kinetics of Fe release from calcareous soils treated with humic acid derived from pudrite (HAP) after 1440 min

Addition of Fe after HA (B treatment), led to increasing Fe desorption through the entire reaction time regardless of the source of the applied humic acid. After 2 months of incubation, Fe desorption from S1 increased from about 2 $mg\ kg^{-1}$ in control treatment to 18.5 and 19.5 $mg\ kg^{-1}$ in B treatments (addition of Fe after HAP and HAC, respectively). It is worthy to mention that the respective values were 17.3, 18.5 and 17.8, 18.7 $mg\ kg^{-1}$ for S2 and S3.

Results depicted in Figure (1) reveal that rate of Fe desorption due to C treatment (addition of Fe before HAs) was significantly higher compared to desorption of Fe due to A&B treatments. The rates of desorbed Fe increased to

24 and 26 $mg\ kg^{-1}$ in S1 and S2, respectively. Application of Fe before HA, caused more Fe sorption, consequently less desorption was expected compared to control. Also, increasing of desorption may be due to decreasing the pH of the soils and consequently increasing Fe desorption.

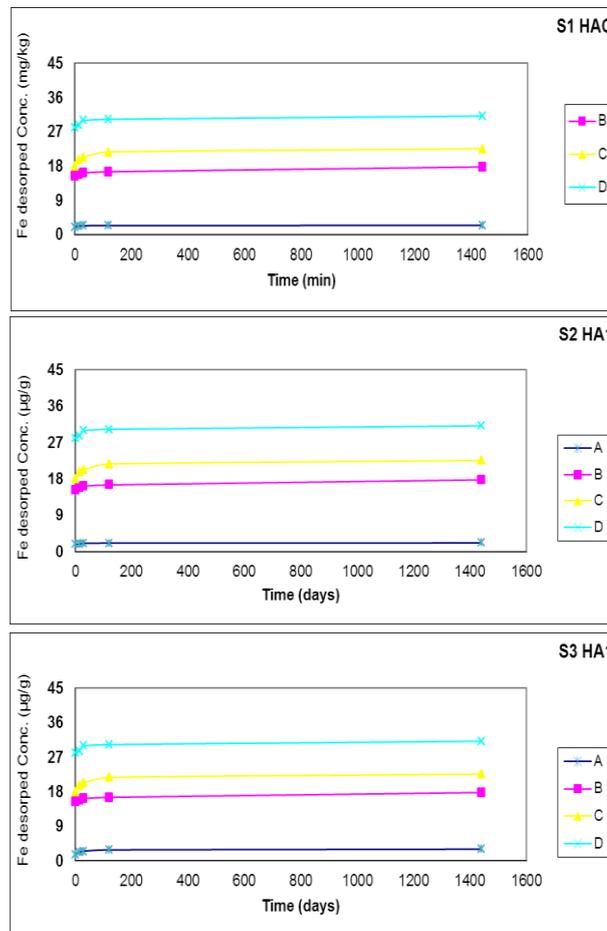


Figure 2. Kinetics of Fe release from calcareous soils treated with humic acid derived from clover compost (HAC) after 1440 min.

The mixture of HAP or HAC with Fe applied to S1 (D treatment) gave the highest Fe desorption compared to other treatments, where the Fe desorbed after two months of application of the HAs mixture to the used soils increased desorbed Fe to 35 and 40 $mg\ kg^{-1}$.

Effect of the applied humic acid coating materials on the constants of the models used to describe Fe desorption from the studied calcareous soils.

Table (4) represents the constants of MFE, the model succeeded for describing the kinetic data since it had high significant R^2 values ranged between 0.89** - 0.99** for S1, 0.90** - 0.96** for S2 and 0.81** - 0.99** for S3, and at the same time gave low standard error values ranged between 0.002-0.046 for all the studied soils and for both the applied humic acids.

The application of Fe individually to the used calcareous soils (A treatment) gave the lowest values of Fe desorption rate. Numerically, the rate of Fe release from S1 due to A treatment was 0.0078 $mg\ kg^{-1}\ min^{-1}$, which represents the lowest value compared with the other treatments applied, the corresponding values of other soils under the same treatment were 0.019 and 0.02 $mg\ kg^{-1}\ min^{-1}$ for S2 and S3 respectively.

Results in the same Table showed that application of humic acid before Iron Fe (B treatment) significant increased the rate of Fe desorption from the studied soils. Table 4 showed that application of B treatment to S1 increased Fe release from 0.0078 mg kg⁻¹ min⁻¹ in control A treatment to

0.0213 and 0.0552 mg kg⁻¹ min⁻¹ in S1HAP and S1HAC respectively. In other words, application of B treatment to S1 increased Fe desorption from calcareous soils regardless the type of humic acid applied. The same trend was observed than other used soils under both sources of HAs.

Table 4. Constants of MFE described Fe release from different soils as affected by methods of HA applied to calcareous soils

	HAP				HAC			
	S1				S2			
	a	b	R ²	SE	a	b	R ²	SE
A	0.0078	0.312	0.96**	0.002	0.0078	0.31	0.99**	0.002
B	0.0213	1.213	0.98**	0.014	0.0552	1.22	0.95**	0.024
C	0.0580	1.247	0.89**	0.023	0.0864	1.24	0.91**	0.033
D	0.0613	1.436	0.92**	0.033	0.0971	1.46	0.94**	0.020
	S2				S3			
	a	b	R ²	SE	a	b	R ²	SE
A	0.019	0.154	0.90**	0.046	0.019	0.154	0.94**	0.014
B	0.039	1.182	0.95**	0.010	0.045	1.210	0.92**	0.016
C	0.053	1.246	0.93**	0.017	0.065	1.250	0.96**	0.015
D	0.063	1.428	0.96**	0.009	0.090	1.446	0.94**	0.009
	S3				S3			
	a	b	R ²	SE	a	b	R ²	SE
A	0.02	0.16	0.96**	0.04	0.02	0.17	0.99**	0.02
B	0.03	1.18	0.81**	0.02	0.04	1.21	0.89**	0.01
C	0.16	0.16	0.96**	0.04	0.07	1.24	0.91**	0.03
D	0.18	1.44	0.88**	0.01	0.16	1.45	0.95**	0.01

Application of Fe before HA in calcareous soils (C treatment), influenced Fe desorption from the studied calcareous soils. Results showed that application of HAC to S1 (C treatment) significantly increased Fe desorption to 0.0864 mg kg⁻¹ min⁻¹, to be higher than A or B treatments applied to calcareous soils. It should be noted that the corresponding values were 0.065 and 0.07 mg kg⁻¹ min⁻¹ in S2 and S3 respectively. These values of S2 and S3 perhaps due to decreasing CaCO₃ content in these soils compared to S1. In other words, increasing the rate of Fe desorption inversely correlated with decreasing the CaCO₃ content in used soils. The same trend was observed in HAP applied to calcareous soils.

treated with HAP, increased the rate of Fe desorption from 0.0078 mg kg⁻¹ min⁻¹ in control to 0.0613 mg kg⁻¹ min⁻¹, the corresponding values for HAC applied to S1 were 0.0078 in control increased to 0.0917 mkg⁻¹ min⁻¹, the same trend was also observed in other soils used.

Application of D treatment represented the mixture between Fe and HA applied to used soils, results showed that this treatment gave the highest rate values regardless the type of humic acid applied. Application of D treatment to S1

Results in the Table (5) indicated that the Elovich model well described the kinetic data by having significant R² and reasonable standard error SE values. The rate of Fe desorption significantly influenced by treatments applied in calcareous soils. Again, the application of Fe individually gave the lowest values in all soils. In general, results showed that again application of D treatment in calcareous soils treated with HAP or HAC gave the highest values compared with B or C treatments. Also, the calcareous soils didn't treat with HAs (A treatment) gave the lowest values according to the interaction Fe with calcareous soils.

Table 5. Constants of Elovich equation described Fe release from different soils as affected by methods of HA applied to calcareous soils

	HAP				HAC			
	S1				S2			
	a	b	R ²	SE	a	b	R ²	SE
A	0.0064	2.05	0.96**	0.01	0.0064	2.05	0.99**	0.01
B	0.0389	16.31	0.96**	0.05	0.0801	16.45	0.95**	0.09
C	0.0648	17.56	0.88**	0.02	0.0187	17.33	0.90**	0.07
D	0.0938	20.05	0.99**	0.01	0.0215	27.49	0.91**	0.20
	S2				S3			
	a	b	R ²	SE	a	b	R ²	SE
A	0.23	1.39	0.87**	0.25	0.23	1.75	0.93**	0.07
B	0.64	15.19	0.94**	0.44	0.82	16.18	0.91**	0.73
C	0.96	17.56	0.92**	0.85	0.88	17.67	0.95**	0.82
D	1.06	26.74	0.95**	0.61	1.33	27.91	0.93**	0.67
	S3				S3			
	a	b	R ²	SE	a	b	R ²	SE
A	0.34	1.39	0.93**	0.25	0.34	1.43	0.97**	0.15
B	0.45	15.06	0.80**	0.65	0.45	16.27	0.88**	0.46
C	1.45	17.65	0.92**	0.82	0.98	17.38	0.89**	1.39
D	1.13	27.80	0.87**	0.69	0.65	27.85	0.94**	0.75

Concerning the type of humic acids, application of humic acid2 (HAC) to the soils give values higher than that treated with HAP. Results in the same table indicated that

increasing calcium carbonate content generally decreased the rate of Fe desorption.

Results in Table (6) showed that Parabolic diffusion model well described the kinetic data by having high R² values 0.91** and 0.99** with reasonable SE varied

between different soils and ranged between 0.01 and 0.64. These values imply that diffusion phenomena-controlled desorption of Fe from the treated soil system.

Table 6. Constants of PDE described Fe release from different soils as affected by methods of HA applied to calcareous soils

	HAP				HAC			
	a	b	R ²	SE	a	b	R ²	SE
	S1							
A	0.51	2.05	0.95**	0.01	0.05	2.02	0.98**	0.03
B	0.27	15.99	0.91**	0.39	0.40	15.87	0.93**	0.07
C	0.81	16.85	0.96**	0.69	1.27	16.28	0.97**	0.95
D	0.97	25.99	0.86**	1.78	1.41	27.69	0.94**	0.15
	S2							
A	0.16	1.24	0.97**	0.13	0.16	1.71	0.98**	0.04
B	0.43	14.89	0.99**	0.16	0.55	15.75	0.97**	0.40
C	0.63	17.08	0.99**	0.15	0.59	17.08	0.99**	0.15
D	0.87	26.31	0.99**	0.16	0.87	27.47	0.99**	0.28
	S3							
A	0.22	1.23	0.99**	0.10	0.22	1.30	0.99**	0.03
B	0.32	14.74	0.91**	0.45	0.31	16.00	0.97**	0.23
C	0.45	17.14	0.98**	0.37	0.75	16.52	0.98**	0.64
D	0.65	27.40	0.96**	0.38	0.98	27.32	0.99**	0.20

The rate constant *a* of diffusion models showed that application of Fe individually to soils gave the lowest values in all used soils. For example, the rate of Fe desorption from S2 untreated with HAP (A treatment) was 0.16 mg kg⁻¹ min⁻¹, this value increased to 0.43, 0.63 and 0.87 mg kg⁻¹ min⁻¹ for B, C and D treatments respectively. Again, results showed that the application of D treatment gave the highest values in all soils used. Application of D treatment in S3 treated with HAP reached to 0.65 mg kg⁻¹ min⁻¹. Application of B and C treatments, however, gave rate values equal to 0.32 and 0.45 mg kg⁻¹ min⁻¹. Worth to mention that the same trend was observed in other soils treated with HAC.

The effect of active CaCO₃ contents in used soils influenced the rate constants of PDE. The rate constant *a* of diffusion model in S1 treated with HAC (D treatment) was 1.41 mg kg⁻¹ min⁻¹, this value decreased to 0.87 and 0.98 mg kg⁻¹ min⁻¹ for S2 and S3 respective to be barreled with decreasing active CaCO₃ in used soils.

Like other models used, there was a significant variation between the two types of HA used in release of Fe from used soils. Results in the same table showed that in S3, for example, the rate of Fe desorption from the soils was 0.98 mg kg⁻¹ min⁻¹ in D treatment using HAC, this value decreased to 0.65 mg kg⁻¹ min⁻¹ using HAP, the same trend was observed in other treatments applied and in all used soils. This result perhaps represents the significant variation between the two types of HA used in this work in coating CaCO₃ particles as a barrier between Fe applied and CaCO₃ particles. In other words, increasing the thickness of coating significantly increased the rate of Fe desorption and other elements could be found in the same system (Ammari, *et al.*, 2015). Accordingly, HAC had a molecular weight higher than HAP and had the opportunity to retain ions in the ecosystem and could be preferable to be applied in calcareous soils.

Kinetics of Mn release from calcareous soils as affected by type and methods of humic acids application

Manganese is an essential micronutrient for plant growth (Hansen *et al.* 2006; Rombolà and Tagliavini 2006)

and its deficiency limits plant growth and decreases crop yield (Thomine and Lanquar 2011; Walker and Connolly 2008). Also, the low input of Mn in the human diet causes serious health problems for human, Mn deficiency anemia IDA, which reduces work productivity of manual laborer, and is particularly the main reason for maternal mortality (ADB 2010).

Results depicted in Figure (3) showed that application of Manganese (Mn²⁺) individually (A) to all calcareous soils gave the lowest values of Mn desorption from selected soils through the entire reaction time. Numerically, the range of Mn desorption ranged between 2.1 and 2.3 mg kg⁻¹ soil. Sorption reactions on the soil-water interface take part in controlling the ion availability in soil (Abbas, and Salem 2011). Calcium carbonate increased Mn sorption in calcareous soil (Hassan, 2012).

Addition of Mn after HA (B treatments), led to increase Mn desorption through the entire reaction time in both HA treatments. After 2 months of treated soils incubation, data showed that Mn desorption from S1 increased from about 2 mg kg⁻¹ in control to 18.5 and 19.5 mg kg⁻¹ for HAP and HAC respectively, it should be mention that the corresponding values were 17.3, 18.5; and 17.8, 18.7 mgkg⁻¹ for S2 and S3 respectively.

In C treatment (addition of Mn before HA), results showed that the rate of Mn desorption significantly increased compared to A&B treatments applied. Results depicted in the same figure showed that the rate of Mn increased to 24 and 26 mg kg⁻¹ in S1 and S2 respectively. Although application of Mn before HA was expected to show lower desorbed Mn values compared to A and B treatments, yet decreasing the pH of the soil ecosystem significantly led to increasing Mn desorption.

The mixture treatment of HAP and Mn (D treatment) applied to S1 gave the highest Mn desorption compared to the other treatments. Results showed that after two months, application of mixture treatment to the other used soils increased Mn desorption to 35 and 40 mg kg⁻¹ to outperform the other treatments added to the calcareous soils. It should be mentioned that the same trend was also observed with the other applied humic acid (HAC) and the other used soils.

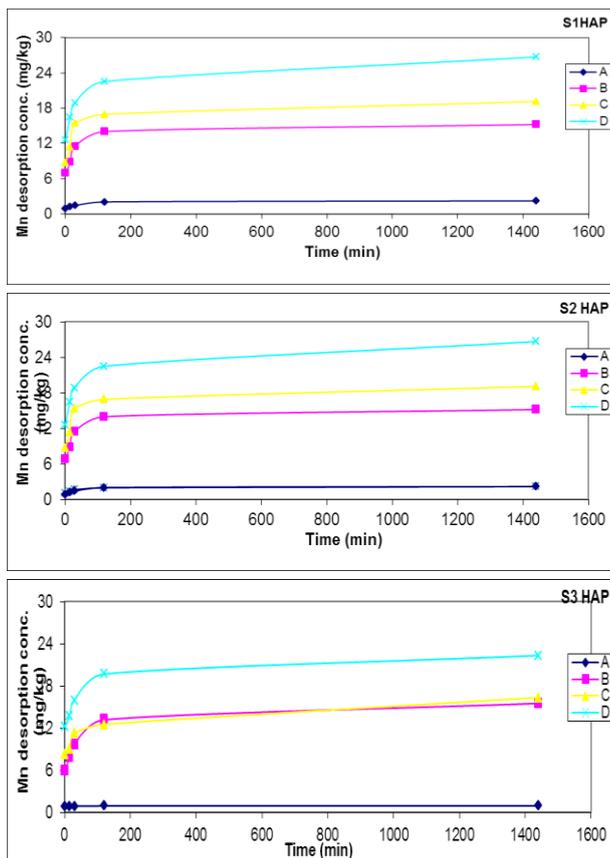


Figure 3. Kinetics of Mn release from calcareous soils treated with humic acid derived from pudrite (HAP) after 1440 min

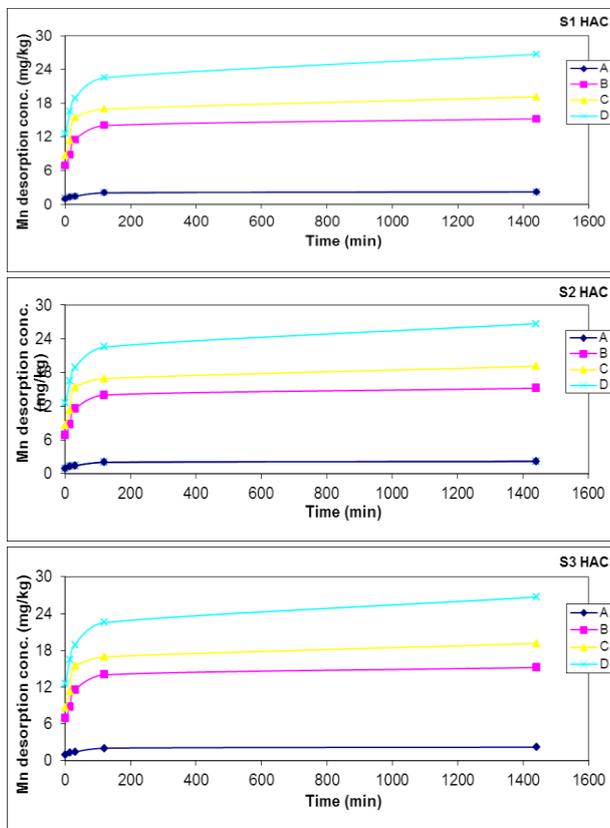


Figure 4. Kinetics of Mn release from calcareous soils treated with humic acid derived from clover compost (HAC) after 1440 min.

Effect of humic acid coating materials applied on the rate constants of used models describe Mn desorption from calcareous soils

Table (7) revealed that Modified Freundlich equation well described Mn desorption by having significant R^2 ranged between 0.94** - 0.99** in S1, 0.94** - 0.99** in S2 and 0.97** - 0.99** in S3, besides having low standard error ranged between 0.01-0.04 in all soils. The good fitting of MFE in describing desorption of Mn process was previously mentioned by Moharami and Jalali (2013).

Concerning the equation constant, (a) different treatments for all the studied soils were highest, generally, due to the D treatment whereas the lowest ones were obtained due to the A treatment.

Numerally the a values of S1 treated with HAP, results showed that a constant was increased from 0.10 in A treatment to 0.33 $\text{mg kg}^{-1} \text{min}^{-1}$ in D treatment (a mixture of humic acid with manganese), while application of both B or C treatment gave middle values. Also, in all cases application of Mn after humic acid (B treatment) gave higher values than C treatment, equal to 0.45, 0.31 in S1- HAP, 0.58, 0.39 in S₂ HAP and 0.65, 0.51 in S3 HAP.

The comparison between the two humic acids applied implies the type of HA applied influenced by CaCO_3 content in used soils. In other words, the rate of Mn desorbed from the S1 increased in the case of HAC applied compared to HAP, for example, in D treatment the rate values were 0.41 decreased to 0.33 $\text{mg kg}^{-1} \text{min}^{-1}$. Decreasing the CaCO_3 content in S₂, almost gave the same previous trend. However the significant decreasing of CaCO_3 content in S3, led to an increase in the rate of Mn desorption in HAP more than HAC. Increasing of CaCO_3 in used soil may led to catch the organic components of HAP comparing to HAC and also led to decrease the thickness of the coating, consequently the rate of Mn desorption was decreased according to expected interaction between Mn and CaCO_3 particles, and vice versa, decreasing CaCO_3 content in used soils led to increase the coating of HA and increasing the rate of Mn desorption as shown in S3. In conclusion, in the presence of high CaCO_3 content in the soil HAC was preferable to be applied and in the case of decreasing CaCO_3 content HAP should be used for increasing the rate of both Fe and Mn desorption from calcareous soils.

Elovich equation

Results in Table (8) showed that Elovich equation also gives high and significant R^2 ranged between 0.88** - 0.99** for all soils treated with HAP and range between 0.90** - 0.99** in all soils treated with HAC, also the standard error values were low enough to say that this model well described the kinetic data.

Application of D treatment, again gave the highest value in most cases compared to other treatments applied. Application of D treatment in S3 HAP was 4.98 $\text{mg kg}^{-1} \text{min}^{-1}$, however, application of B treatment (Mn after humic acid) gave rate equal to 2.83 $\text{mg kg}^{-1} \text{per min}^{-1}$. The corresponding value of S2 HAC treated with B treatment was 2.39 $\text{mg kg}^{-1} \text{per min}$. Like modified Freundlich equation, application of humic acid was preferable to increase the rate of Mn desorption, numerically in S3 HAC in C treatment, the rate of Mn desorption was 2.26 $\text{mg kg}^{-1} \text{per min}^{-1}$, this value increased to 3.64 $\text{mg kg}^{-1} \text{per min}^{-1}$ in S3HAP. The same trend was also observed in other soils used.

The CaCO_3 content in used soil significantly influenced the rate of Mn desorption. increasing of CaCO_3 in S1 B treatment in HAP decreased the rate of Mn desorption to 0.39 $\text{mg kg}^{-1} \text{min}^{-1}$ by decreasing both total and active calcium carbonate in S3 the rate of Mn desorption increased to 2.83 $\text{mg kg}^{-1} \text{per min}^{-1}$ in S3HAP

Table 7. Rate constants of MFE described Mn release from different soils as affected by methods of HA applied to calcareous soils

	HAP				HAC			
	S1							
	a	b	R ²	SE	a	b	R ²	SE
A	0.10	-0.09	0.94**	0.01	0.10	-0.39	0.97**	0.04
B	0.45	0.41	0.99**	0.03	0.39	0.53	0.99**	0.01
C	0.31	0.65	0.97**	0.03	0.39	0.63	0.99**	0.02
D	0.33	0.31	0.99**	0.02	0.41	0.80	0.98**	0.03
S2								
	a	b	R ²	SE	a	b	R ²	SE
A	0.37	-0.31	0.99**	0.02	0.36	-0.29	0.94**	0.05
B	0.58	0.11	0.99**	0.03	0.49	0.29	0.99**	0.02
C	0.39	0.45	0.97**	0.04	0.46	0.44	0.99**	0.03
D	0.35	0.68	0.99**	0.02	0.40	0.67	0.98**	0.03
S3								
	a	b	R ²	SE	a	b	R ²	SE
A	0.39	0.10	0.99**	0.01	0.39	0.10	0.97**	0.04
B	0.65	0.27	0.99**	0.03	0.44	0.42	0.99**	0.01
C	0.51	0.55	0.97**	0.03	0.42	0.54	0.99**	0.02
D	0.81	0.75	0.99**	0.02	0.38	0.74	0.98**	0.03

Table 8. Constants of Elovich model describe Mn release from different soils as affected by methods of HA applied to calcareous soils

	HAP				HAC			
	S1							
	a	b	R ²	SE	a	b	R ²	SE
A	0.10	-0.09	0.94**	0.01	0.10	-0.39	0.97**	0.04
B	0.39	0.41	0.99**	0.03	0.45	0.53	0.99**	0.01
C	0.31	0.65	0.97**	0.03	0.39	0.63	0.99**	0.02
D	0.35	0.31	0.99**	0.02	0.81	0.80	0.98**	0.03
S2								
	a	b	R ²	SE	a	b	R ²	SE
A	0.41	-0.313	0.99**	0.02	0.41	-0.39	0.97**	0.04
B	0.582	0.114	0.99**	0.03	0.39	0.53	0.99**	0.01
C	0.388	0.451	0.97**	0.04	0.39	0.63	0.99**	0.02
D	0.353	0.683	0.99**	0.02	0.35	0.80	0.98**	0.03
S3								
	a	b	R ²	SE	a	b	R ²	SE
A	0.016	0.888	0.91**	0.01	0.016	0.368	0.90**	0.26
B	2.832	1.940	0.89**	2.01	2.635	3.392	0.93**	1.39
C	3.635	4.797	0.94**	1.39	2.264	4.507	0.95**	1.48
D	4.983	7.832	0.88**	2.32	2.067	7.227	0.92**	2.42

Parabolic diffusion equation (PDE):

Table 9 implies the possibility of using PDE to describe the kinetic data by having significant high R² ranged between 0.83** - 0.99** and low standard error (SE) ranged between 0.005 - 2.42. The relatively high SE values perhaps imply that the diffusion model could be arranged

after MFE and Elovich models. The rate constants of PDE seemed to be highest due to the treatment D in all the investigated sites. Both *a* and *b* values were, generally, high due to the application of HAC or HAP. The treated A resulted in the lowest *a* and *b* values in all soils regardless of the type of humic acid applied.

Table 9. Constants of PDE describe Mn release from the different soils as affected by methods of HA applied to calcareous soils

	HAP				HAC			
	S1							
	a	b	R ²	SE	a	b	R ²	SE
A	0.031	1.013	0.99**	0.00	0.150	0.898	0.89**	0.25
B	1.194	6.016	0.92**	1.70	1.096	7.338	0.95**	1.15
C	0.919	8.392	0.86**	1.82	1.352	9.128	0.96**	1.22
D	1.261	12.040	0.91**	2.00	1.706	12.571	0.94**	1.97
S2								
	a	b	R ²	SE	a	b	R ²	SE
A	0.341	0.657	0.94**	0.16	0.400	0.369	0.90**	0.26
B	2.832	0.841	0.89**	2.01	2.635	2.293	0.93**	1.39
C	2.156	3.936	0.83**	2.05	3.264	3.408	0.95**	1.48
D	2.983	6.734	0.87**	2.32	4.067	6.128	0.92**	2.42
S3								
	a	b	R ²	SE	a	b	R ²	SE
A	0.007	0.905	0.93**	0.00	0.169	0.773	0.93**	0.22
B	1.194	4.759	0.92**	1.70	1.096	6.081	0.95**	1.15
C	0.919	7.135	0.86**	1.82	1.352	7.871	0.96**	1.22
D	1.261	10.783	0.91**	2.00	1.706	11.314	0.94**	1.97

Discussion:

In this work, either of two types of humic acid were applied (HAP and HAC) to three types of calcareous soils varying in their calcium carbonate contents to minimize the fixation of both Fe and Mn on calcium carbonate found in these soils. The minimizing of fixation based on the addition of HA to used soils represented in three treatments B, C and D treatments beside A treatment as A control without humic acid application.

Results of this work implied significant variations between the different soils in both Fe and Mn desorption mainly due to calcium carbonate contents. In other words, increasing calcium carbonate content, significantly decreased the concerned metal desorption based on the creation of complexed compound between calcium carbonate and these metals. Application of humic acid, significantly increased the rate of ions desorption from used soils. These materials i.e. HAP and HAC probably acted as a barrier between calcium carbonate particles and Fe or Mn ion(s) studied. Thus led to increase desorption of these ions rate values depending on the type of added HA and their time of application.

For more explanation, application of Fe or Mn after humic acid (B treatment) was more preferable in increasing desorption of the considered ions compared to C treatment (addition of Fe or Mn before humic acid). These results were reasonable because the application of ions before humic acid led to increasing the interaction or fixation of these ions with calcium carbonate particles, the application of humic acids didn't significantly increase the rate of desorption at C treatment. Of all treatments the addition of a mixture of either of these ions with humic acid was the treatment of the best effect on desorption of Fe or Mn from the studied calcareous soils.

The kinetic models used represented by MFE, Elovich and PDE were succeeded in describing the kinetic data. Saber *et al.*, (2012) mentioned that the success of more than one model describing the kinetic data means that there is more than one mechanism take place in desorption of Mn and Fe treated calcareous soils.

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تأثير حمض الهيوميك على صور الحديد والمنجنيز في بعض الأراضي الجيرية

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قسم كيمياء وطبيعة الاراضي مركز بحوث الصحراء

تحتوى الاراضى الجيرية على نسبة عالية من كربونات الكالسيوم سواء الكلبة أو الفعالة تؤدي الى تثبيت معظم العناصر الضرورية لنمو النباتات المنزرعة في هذه الاراضى وتجعلها في صورة غير ميسرة ومن أهم العناصر الصغرى التى لها فاعل وتتأثر بشكل مباشر بحبيبات كربونات الكالسيوم عنصرى الحديد والمنجنيز. ويهدف هذا البحث الى تقييم تقنية تغليف حبيبات كربونات الكالسيوم بنوعين من حامض الهيوميك العضوى لهما صفات مختلفة تم تناولها في هذا البحث ، أضيفا بطرق مختلفة مع العنصرين تحت الدراسة فى ثلاثة أنواع من الاراضى الجيرية المختلفة فى محتواها من كربونات الكالسيوم النشط وأستمرت التجربة لمدة شهرين . بعد مرور شهرين اظهرت النتائج المتحصل عليها الاتى: -أوضحت الدراسة الكينيتيكية أن كافة المعادلات المستخدمة نجحت فى وصف التفاعلات المختلفة فى نظام الاراضى الجيرية - حامض الهيوميك - الحديد أو المنجنيز وبالتالي يمكن الأعتقاد على ثوابت هذه المعادلات فى وصف التفاعلات المختلفة-أضافة عنصرى الحديد والمنجنيز الى الاراضى الجيرية بدون أضافة الهيوميك كان لة تأثير معنوى فى تثبيت العنصرين بطرق مختلفة أظهرته الدراسة الكينيتيكية التى أجريت فى هذا البحث-أضافة أى من العنصرين قبل حامض الهيوميك أدى الى زيادة طفيفة ولكن معنوية مقارنة بالكنترول (الاراضى الغير معاملة بالهيوميك) فى أنطلاق أى من العنصرين من الاراضى المعاملة-أضافة أى من العنصرين بعد حامض الهيوميك أدى الى زيادة أعلى من المعاملة السابقة نظرا لعمل حامض الهيوميك كحاجز بين حبيبات كربونات الكالسيوم مع أى من العنصرين-أظهرت الدراسة الكينيتيكية أن أضافة أى من العنصرين مخلوطا بأى من حامضى الهيوميك أدى الى أعلى أنطلاق أى من كلا العنصرين من الاراضى المعاملة -مقارنة كل من نوعى حامض الهيوميك أظهرت أن هناك فروق معنوية بين كلا النوعين فى أنطلاق العناصر تحت الدراسة -تمت مناقشة كافة الميكانيكيات فى نظام الاراضى الجيرية - حامض الهيوميك - الحديد أو المنجنيز والتى أدت الى أختلاف أنطلاق العناصر المدروسة