

## **ASSESSMENT OF PHOSPHORUS DESORPTION IN SOME FULVIC ACID-TREATED EGYPTIAN SOILS**

Zaghloul, A.\*; M.A. Abou-Seeda\*\* and H.I. El-Aifa\*\*

\* Soils and Water Use Dept. National Res. Centre, Dokki, Giza, Egypt.

\*\* Plant Nutrition Dept. National Res. Centre, Dokki, Giza, Egypt.

### **ABSTRACT**

Kinetic of phosphate release in soils has drawn a considerable attention in recent years. Soluble organic matter plays an important part in phosphate release. Effect of fulvic acid (FA) on phosphate desorption was investigated. Results revealed that power function (modified Freundlich), two sites and zero-order kinetic equations gave a highly significant ( $R^2$ ) mostly in all cases in different treatments of monocalcium phosphate (MCP) and (FA) treated soils. It was observed that rate coefficients of phosphate desorption ( $K_d$ ) in sandy soil were gradually increased with P.fertilizer added as compared with other treatments. Results also revealed that application of fulvic acid to soil decreased the P-desorption particularly in alluvial soil. Fulvic acid treated soil resulted in a reduction of P-desorption and also regulated the releaseable fraction of phosphorus in soils. It was noticed that for the entire reaction period, alluvial clay soil can be able to supply P to cultivated media as compared with other investigated soils. Results also showed that the supplying power of FA treated soils was almost emphasized over the uncoated SP treated soils. These result may be related to the role of FA for increasing the supplying power due to chelation reaction.

### **INTRODUCTION**

Organic manure being considered as plant growth regulator can play an important role in modern agriculture and turf management. The application of these materials is an important aspect to sustain soil productivity and to maintain beneficial soil biological, chemical and physical properties (Abou Seeda, 1987). Phosphorus Fertilizer accumulates in the surface layer of soils and can be strongly sorbed or participated in the soil (Sharply and Ahuja, 1982), but phosphorus can leached in areas of high peontent (Sayin, et al., 1990).

Moreover, humic substances are the most widespread and ubiquitous natural nonliving organic materials in all terrestrial and aquatic environments, and represent significant proportion of total organic C. Humic substance can be divided into humic acid (HA) and fulvic acids (FA), the portion that is soluble at any pH value even below 2 (Sparks, 1998). The kinetic reaction of such heterogeneous mixture compounds with plant macronutrients in soil systems is limited.

The ability of some organic anions to form stable complexes with iron and aluminum oxihydroxides of soils and therefore to enhance the solubility of phosphate in most soils has been widely reported by (Barrow and Shaw (1975)). The effectiveness of organic anions in influencing phosphorus

solubility is related to the structure of the organic molecule and the pH of the system (Sparks, 1998).

The release of phosphate increases with increasing the concentration of organic anion in solution (Sparks, 1989). Understanding the modeling factors, which affect the biomass production in Egyptian soils, has created the need to quantify and maximize the flux of indigenous soil phosphate between the soil matrix and soil solution.

Methodologies applied in most reported kinetic of soil chemical process studies involved resin technique (Amer, et.al., 1955 and Zaghloul, 1998), batch technique (Evan and Jurinak, 1976; Havlineand Westfall, et.al.,1985) and Flow technique (Sparks and Jurdin, 1984; Zaghloul and El-Ashry, 2000). The results from batch method studies are influenced by several disadvantages like method of separation of adsorbate from solution. Electrical stirred Flow unit (ESFU) has several advantages over batch technique (Zaghloul and El-Ashry, 2000). The objective of this study is to select the best theoretical and empirical models using *ESFU* to examine the effect of fulvic acid (FA) on phosphate release kinetics from different Egyptian cultivated soils.

## MATERIALS AND METHODS

### Soils

The soils used in this study are alluvial clay soil (*Typic torrerts*), Calcareous soil (*Typic calcids*) and sandy soil (*Typic psammments*). The collected soils were air-dried and screened through a 2-mm sieve. Some physical and chemical properties of the investigated soils are presented in Table (1).

In each soil types, 200g of soil samples were treated as follow:

- A:** no treatment,                      **B:** 200ml fulvic acid treatment free of superphosphate  
**C:** 0.5g calcium superphosphate      **D:** 200 ml fulvic acid incorporated with 0.50g superphosphate and  
**E:** 0.5g superphosphate incorporated with the soil samples and then treated with 200m fulvic acid.

Each treatment was triplicated and incubated at room temperature for 2 weeks. The soil samples were then ground, crushed and prepared for the kinetic studies.

**Table (1): Some physical and chemical characteristics of the studied soils.**

Properties	Clay soil	Calcareous soil	Sandy soil
Sand %	14	42	89.36
Silt %	24	30	5.51
Clay %	62	28	5.13
pH (1:2.5)	8.2	8.5	8.00
ECe (dSm <sup>-1</sup> )	0.3	0.35	0.44
OM%	0.46	0.30	0.04
CaCO <sub>3</sub> %	5.41	16.21	3.61
CEC (meq/100g)	51.92	22.63	4.49
Available P (ppm)	20.12	10.40	6.3

**Desorption procedures**

Soil samples were kinetically studied using Electrical Stirred Flow Unit (ESFU). About eighty grams of each soil sample were placed in kinetic part of the new setup and mixed with 800ml of 1N Na<sub>2</sub>SO<sub>4</sub> as an extractable soil solution. The device was then mechanically worked and solution samples were taken after 1, 5, 10, 30, 60, 75, 105 and 120 min. Phosphorus was determined by the method described by Cottenie, et.al (1982). These values were plotted as dependent values against time as independent values.

An array of kinetic models including zero-order, first-order, second-order, Elovich, fractional power and two sites equations has been employed to examine the kinetics of phosphate release. The higher coefficient of determination (R<sup>2</sup>) and the lower the (SE) values, the best fitting equation(s) could be used to describe the studied rate phenomena. The mathematical expressions of these models are presented in Table 2.

**Table (2): Different kinetic models used to describe the kinetic data.**

Model	Integrated Form	Reference
Zero-Order	$q_t = kt + b$	
First-Order	$\ln(q_t / q_0) = -k_1 t$ or $q_t = q_0 \exp(-k_1 t)$	Sparks
2 <sup>nd</sup> order	$1/q_t = 1/q_0 + k$	
Fractional Power	$\text{Log } q_t = \log b^1 + k_d \log t$	(1989)
Two sites	$q_t = q_1 \exp(-k_1 t) + q_2 \exp(-k_2 t)$	

Where:  $q_t$  is the amount of P desorbed (mmol/kg) at time  $t$ ,  $q_0$  is the initial amount of P desorbed (mmol/kg) and  $k$ ,  $b$ ,  $b$ ,  $k_d$ ,  $q_1$ ,  $q_2$ ,  $k_1$  and  $k_2$  are constants

In this experiment, the regression analysis was carried out in order to determine the conformity of phosphorus release to specific equation(s). The mathematical equations were investigated by least square regression analysis for phosphorus release in the studied soils. The conventionality of the phosphorus released was based on higher R<sup>2</sup> and lower SE values (Zaghloul, 1998).

**RESULTS AND DISCUSSIONS**

**Conformity of the P release data to the kinetic models**

Table (3) represents the coefficient of determination (R<sup>2</sup>) and the standard error (SE) of the kinetic models used to describe P desorption from the treated soils. It was observed that power function (modified Freundlich), two sites and zero-order kinetic equations, gave highly significant (R<sup>2</sup>) mostly in all cases and in different treatments of MCP (monocalcium phosphate) and FA added to the studied soils.

The coefficient of determination R<sup>2</sup> values were ranged between (0.96<sup>\*\*\*</sup>-0.98<sup>\*\*\*</sup>), (0.86<sup>\*\*\*</sup>-0.98<sup>\*\*\*</sup>), (0.90<sup>\*\*\*</sup>-0.97<sup>\*\*\*</sup>) in alluvial soil; (0.94<sup>\*\*\*</sup>-0.96<sup>\*\*\*</sup>), (0.72<sup>\*\*\*</sup>-0.98<sup>\*\*\*</sup>), (0.84<sup>\*\*\*</sup>-0.97<sup>\*\*\*</sup>) in calcareous soil and (0.95<sup>\*\*\*</sup>-0.99<sup>\*\*\*</sup>), (0.83<sup>\*\*\*</sup>-0.98<sup>\*\*\*</sup>), (0.94<sup>\*\*\*</sup>-0.98<sup>\*\*\*</sup>) in sandy soil for the above mentioned 3 kinetic equations, respectively. However, the lower values of R<sup>2</sup> were noted in control treatments in most cases.

Table (3): Coefficient of determination ( $R^2$ ) and standard error (SE) values for phosphate desorption from P-enriched soils and treated with fulvic acid.

Equation Type	Typic psamments (Soil 1)									Typic Calcids (Soil 2)									Typic torretets (Soil 3)																											
	A1	B1	C1	D1	E1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3	A1	B1	C1	D1	E1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3																
Zero- $R^2$	0.95	0.90	0.93	0.97	0.96	0.93	0.84	0.97	0.96	0.97	0.94	0.97	0.98	0.98	0.98	0.95	0.90	0.93	0.97	0.96	0.93	0.84	0.97	0.96	0.97	0.94	0.97	0.98	0.98	0.95	0.90	0.93	0.97	0.96	0.93	0.84	0.97	0.96	0.97	0.94	0.97	0.98	0.98			
Zero-SE	0.02	0.01	0.14	0.07	0.09	0.02	0.03	0.05	0.06	0.04	0.05	0.03	0.04	0.07	0.07	0.02	0.01	0.14	0.07	0.09	0.02	0.03	0.05	0.06	0.04	0.05	0.03	0.04	0.07	0.07	0.02	0.01	0.14	0.07	0.09	0.02	0.03	0.05	0.06	0.04	0.05	0.03	0.04	0.07	0.07	
1 <sup>st</sup> - $R^2$	0.69	0.079	0.82	0.87	0.90	0.90	0.94	0.93	0.96	0.92	0.85	0.90	0.92	0.89	0.89	0.69	0.079	0.82	0.87	0.90	0.90	0.94	0.93	0.96	0.92	0.85	0.90	0.92	0.89	0.89	0.69	0.079	0.82	0.87	0.90	0.90	0.94	0.93	0.96	0.92	0.85	0.90	0.92	0.89	0.89	
1 <sup>st</sup> -SE	0.09	0.08	0.08	0.09	0.08	0.05	0.06	0.04	0.04	0.05	0.08	0.02	0.02	0.09	0.08	0.09	0.08	0.08	0.09	0.08	0.05	0.06	0.04	0.04	0.05	0.08	0.02	0.02	0.09	0.08	0.09	0.08	0.08	0.09	0.08	0.05	0.06	0.04	0.04	0.05	0.08	0.02	0.02	0.09	0.08	
2 <sup>nd</sup> - $R^2$	0.59	0.64	0.67	0.69	0.75	0.83	0.56	0.85	0.90	0.82	0.72	0.71	0.74	0.72	0.72	0.59	0.64	0.67	0.69	0.75	0.83	0.56	0.85	0.90	0.82	0.72	0.71	0.74	0.72	0.72	0.59	0.64	0.67	0.69	0.75	0.83	0.56	0.85	0.90	0.82	0.72	0.71	0.74	0.72	0.72	
2 <sup>nd</sup> -SE	1.53	2.23	0.22	0.63	0.45	72.0	2.77	0.18	0.29	0.26	0.75	1.15	0.40	0.48	0.42	1.53	2.23	0.22	0.63	0.45	72.0	2.77	0.18	0.29	0.26	0.75	1.15	0.40	0.48	0.42	1.53	2.23	0.22	0.63	0.45	72.0	2.77	0.18	0.29	0.26	0.75	1.15	0.40	0.48	0.42	0.42
Freun.- $R^2$	0.96	0.97	0.97	0.98	0.96	0.89	0.96	0.94	0.84	0.96	0.99	0.97	0.95	0.96	0.96	0.96	0.97	0.97	0.98	0.96	0.89	0.96	0.94	0.84	0.96	0.99	0.97	0.95	0.96	0.96	0.96	0.97	0.97	0.98	0.96	0.89	0.96	0.94	0.84	0.96	0.99	0.97	0.95	0.96	0.96	
Freun.-SE	0.03	0.03	0.02	0.03	0.05	0.05	0.04	0.04	0.08	0.03	0.02	0.04	0.06	0.05	0.05	0.03	0.03	0.02	0.03	0.05	0.05	0.04	0.04	0.08	0.03	0.02	0.04	0.06	0.05	0.05	0.03	0.03	0.02	0.03	0.05	0.05	0.04	0.04	0.08	0.03	0.02	0.04	0.06	0.05	0.05	
Two sites- $R^2$	0.88	0.86	0.97	0.96	0.98	0.87	0.72	0.95	0.98	0.95	0.83	0.94	0.97	0.97	0.98	0.88	0.86	0.97	0.96	0.98	0.87	0.72	0.95	0.98	0.95	0.83	0.94	0.97	0.97	0.98	0.88	0.86	0.97	0.96	0.98	0.87	0.72	0.95	0.98	0.95	0.83	0.94	0.97	0.97	0.98	
Two sites-SE	0.04	0.02	0.54	0.19	0.22	1.14	0.04	0.17	0.07	0.15	0.13	0.07	0.44	0.24	0.25	0.04	0.02	0.54	0.19	0.22	1.14	0.04	0.17	0.07	0.15	0.13	0.07	0.44	0.24	0.25	0.04	0.02	0.54	0.19	0.22	1.14	0.04	0.17	0.07	0.15	0.13	0.07	0.44	0.24	0.25	

\*A= non-treated 200g soils.

B= 200g soils treated with 200ml fulvic acid (F.A.).

C= 200g soils treated with 0.5g monocalcium phosphate (MCP).

D=200g soils treated with 200ml F. A. + 0.5g MCP.

E= 0.5g MCP incorporated with 200g soils then treated with 200ml F.A.

The two sites and zero-order equations showed the highest coefficients of determination at all different treatments, meanwhile, the modified Freundlich equation showed the lowest SE value in all treatments and for all the studied soils. These data suggest that the power function as an empirical equation was the best to describe the kinetic data for different soil types. Nevertheless, the two sites and zero-order equations could be also applied to describe the phosphate kinetics as well. It's generally believed that there is no single equation that describe equally well the desorption kinetic data for all soil samples. Similar results were obtained by Raven and Hossner, (1994).

The parabolic diffusion and Elovich equation did not control the rate of reaction and showed less conformity to describe the kinetic data since they gave lower  $R^2$  and higher SE values. Results also indicated that second-order kinetic equation was almost invalid to describe the kinetic data in most cases, regardless the soil type treatments (data not shown). The results in Table (3) indicate also that higher conformity of desorption data for all five tested kinetic equations was especially observed in calcareous soil treated with fulvic acid.

The fractional-power or modified Freundlich equation, and various modified forms of this equation have been applied to experimental data of phosphorus reactions in soils by several researchers (Cooke, 1966; Kuo and Lotse, 1972 and Elkhatib and Hern, 1988). This empirical equation proved to be the best fitted equation in most cases beside the other types of empirical or theoretical equations that applied also to be fitted with less conformity; such  $n^{\text{th}}$ - order equations are: Elovich and diffusion equations. However, using both of the different empirical or the theoretical equations in kinetics of organic matter (OM) reactions studies are limited as compared with non-organic matter (NOM) studies.

In this study we critically examined, the effect of dividing the entire two-hour-desorption reaction time into two reaction periods, namely, (0-60) min which represents rapid reaction and 1-2 hrs, to represent some of residence time of reaction, to specify whether the rate of reaction takes the same trend through the entire reaction time or could be changed through the time of reaction. Desorption data for each period were fitted to the above named kinetic equations that best describe the kinetic data for the entire reaction time. The coefficient of determination ( $R^2$ ) and (SE) values in the various treatments are shown in Table (4).

Results show in most cases, that dividing the entire reaction time into two stages led to increase of the  $R^2$  values in modified Freundlich equation, the best fitted equation, for both stages and the same trend in second stage for other fitted equations. The  $R^2$  values of the regression line using modified Freundlich equation were increased from 0.84-0.99 in the entire reaction time to 0.96-0.99 and 0.97-0.99 for the first and second stages, respectively. Moreover, the SE values were also decreased from 0.02-0.08 to 0.003-0.01 for the first and second stages in relation to the entire reaction time, respectively. In a few cases, however, the first-order kinetic equation gave similar results in data of second stage of 1-60 min and gave insignificant  $R^2$  at short a period. These results clearly indicate that factors such as reaction period time, the rate and the method of adding fulvic acid (FA)

Table (4): Kinetic parameters of used equations applied to describe the kinetics of phosphate desorption from the studied soils.

Equation Type	Typic psamments (Soil 1)			Typic Calcidis (Soil 2)			Typic Torrents (Soil 3)								
	*A1	B1	C1	D1	E1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3
Zero-	k	0.35	0.10	0.93	0.41	0.37	0.15	0.56	0.47	0.30	0.27	0.17	0.46	0.41	0.48
Ord.	b	0.05	0.063	0.72	0.53	0.06	0.057	0.36	0.34	0.35	0.25	0.24	0.85	0.61	0.68
1 <sup>st</sup>	k <sub>1</sub>	2.80	3.30	3.60	5.20	4.90	3.00	3.00	4.00	3.40	4.20	4.90	5.50	5.30	5.00
Ord.	q <sub>1</sub>	0.85-	1.02-	0.35-	0.41-	0.74-	0.81-	0.24-	0.47-	0.31-	0.56-	0.73-	0.27-	0.36-	0.29-
Modif.	K <sub>d</sub>	0.19	0.31	1.31	0.87	0.76	0.58	1.14	1.00	0.88	0.73	0.57	1.01	1.10	0.96
Freu.	b'	0.22	0.24	0.25	0.35	0.32	0.19	0.29	0.20	0.23	0.29	0.33	0.34	0.35	0.34
Two	K <sub>1</sub>	0.51	0.42	1.30	1.16	0.97	1.14	1.48	1.14	1.50	1.27	1.12	1.58	1.18	1.66
Sites	K <sub>2</sub>	0.03	0.02	0.80	0.92	0.85	0.04	0.29	0.36	0.35	0.13	0.12	1.10	0.55	0.69

\*A= non-treated 200g soils.  
 B= 200g soils treated with 200ml fulvic acid (F.A.).  
 C= 200g soils treated with 0.5g monocalcium phosphate (MCP).  
 D=200g soils treated with 200ml F.A. + 0.5g MCP.  
 E= 0.5g MCP incorporated with 200g soils then treated with 200ml F.A.

treatments, in addition to the soil types, could affect the fitting of the desorption data to a given kinetic equation. Also, the phosphate desorption reaction did not take the same trend through the entire time of reaction, Aharoni, *et al.* (1991) suggested that the kinetics of phosphate sorption/release can successfully be described by an expression that is approximated at beginning times by a fractional-power equation, at intermediate times by the Elovich equation, and at long times by an apparent first-order equation. However, equation(s) arrangement and the best-fitted equation(s) used to describe the rate data in the kinetic studies were mostly affected by number of factors such as pH, clay content, type of clay and different soil properties Fig.(2) which could affect on the availability of the studied ions. The presence of (OM) in soil system could be absolutely change the reactivity of ion(s) in soil systems; this may explain the difference between our results and conclusions in equations arrangement of (Aharoni, *et al.*, 1991).

#### **Soil phosphorus desorption :**

Phosphate in soils undergoes to different reactions with solid phase and thus P-availability may be limited by these reactions despite high residual soil-P due to frequent P-fertilization and indigenous-P. Hence, understanding the nature of these reactions of soil-P and improving fertilization management under different conditions is must. Phosphate desorption from the studied soils revealed that, regardless of soil type the initial reaction of P desorption is fast in the first period (1-60 min) and is followed by a slower reaction for the 2<sup>nd</sup> period (60-120 min). The obtained results show higher values for C treatment, followed by D and then E treatments.

#### **Rate constants describing soil phosphorus desorption kinetics**

##### **1. Entire reaction time**

Typical examples of P desorption kinetic are those of both untreated and fulvic acid-amended soils which depicted in Fig. (1). Obviously, The amount of P release from the studied soil was significantly affected by soil texture and the native P that could be found in these soils. The type of soil components can drastically affect the reaction rate. For example, sorption reactions are often more rapid on clay minerals such as kaolinite and smectites than on vermiculite and subsequently desorption reaction rates that take place (Sparks,1989). Moreover, active CaCO<sub>3</sub> in calcareous soils can take the same order of clay content in alluvial clay soils (Zaghloul,1998).

Results in Table (5) reveal that apparent rate coefficients of phosphate desorption  $k_d$  values in sandy soil were consistently increased with P-fertilizer addition to soil sample coated with or without FA (C<sub>1</sub>, D<sub>1</sub> and \*E<sub>1</sub> + treatments) in relation to control sandy soil (A<sub>1</sub>) or sand soil coated with (FA) depending on native P (B<sub>1</sub> treatment). Data in the same table showed also that rate of P desorption from alluvial soil treated with super-P (C<sub>1</sub>) was consistently increased over control treatments and over D<sub>3</sub> (P-FA treated soils) or E<sub>3</sub> (FA-P treated soil). The mean values of  $k_d$  in control treatments are 0.19 and 0.31 mg kg<sup>-1</sup>soil min<sup>-1</sup> in A<sub>1</sub> and B<sub>1</sub>. These values almost duplicate and triplicated to be 0.87 and 0.96-mg kg<sup>-1</sup>soil min<sup>-1</sup> in D<sub>1</sub> and E<sub>1</sub> and reached 1.31mg kg<sup>-1</sup>soil min<sup>-1</sup> in C<sub>1</sub>. However, the capacity factor  $b^1$  of

Table (5): Coefficient of determination R<sup>2</sup> and Standard error (SE) of the kinetic equation that describe P-release from the studied soils at different reaction period

Soil	Tret	Zero-order equation						1 <sup>st</sup> . Order equ.						M. Freundlich equ						Two sites equ					
		1 <sup>st</sup> . period		2 <sup>nd</sup> . Period		1 <sup>st</sup> . period		2 <sup>nd</sup> . Period		1 <sup>st</sup> . period		2 <sup>nd</sup> . Period		1 <sup>st</sup> . period		2 <sup>nd</sup> . Period		1 <sup>st</sup> . period		2 <sup>nd</sup> . period					
		R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE	R <sup>2</sup>	SE				
Typic	A1	0.92	0.03	0.98	0.002	0.60	0.11	0.78	0.01	0.92	0.05	0.99	0.003	0.85	0.05	0.80	0.01	0.85	0.05	0.80	0.01				
	B1	0.72	0.02	0.94	0.005	0.62	0.12	0.94	0.01	0.96	0.03	0.99	0.003	0.78	0.01	0.86	0.01	0.78	0.01	0.86	0.01				
	C1	0.72	0.23	0.99	0.03	0.62	0.11	0.98	0.01	0.96	0.04	0.99	0.005	0.74	0.05	0.99	0.29	0.74	0.05	0.99	0.29				
Psam.	D1	0.92	0.08	0.99	0.04	0.78	0.12	0.98	0.01	0.97	0.03	0.98	0.009	0.92	0.16	0.97	0.12	0.92	0.16	0.97	0.12				
	E1	0.86	0.11	0.98	0.06	0.75	0.11	0.99	0.01	0.99	0.02	0.96	0.01	0.85	0.22	0.99	0.20	0.85	0.22	0.99	0.20				
	A2	0.72	0.02	0.85	0.02	0.67	0.06	0.84	0.03	0.96	0.02	0.90	0.03	0.63	0.03	0.74	0.03	0.63	0.03	0.74	0.03				
Typic	B2	0.72	0.03	0.95	0.005	0.68	0.01	0.90	0.01	0.94	0.06	0.95	0.01	0.63	0.05	0.94	0.008	0.63	0.05	0.94	0.008				
	C2	0.81	0.07	0.98	0.03	0.75	0.06	0.94	0.02	0.98	0.02	0.98	0.009	0.78	0.16	0.96	0.13	0.78	0.16	0.96	0.13				
	D2	0.86	0.04	0.99	0.01	0.79	0.05	0.96	0.02	0.99	0.01	0.99	0.01	0.80	0.08	0.99	0.07	0.80	0.08	0.99	0.07				
Cacid.	E2	0.87	0.06	0.996	0.009	0.80	0.06	0.99	0.004	0.99	0.02	0.99	0.007	0.84	0.14	0.99	0.05	0.84	0.14	0.99	0.05				
	A3	0.89	0.05	0.98	0.02	0.79	0.09	0.92	0.01	0.99	0.02	0.93	0.01	0.85	0.09	0.82	0.06	0.85	0.09	0.82	0.06				
	B3	0.86	0.04	0.99	0.01	0.74	0.11	0.96	0.02	0.99	0.01	0.98	0.02	0.80	0.06	0.96	0.05	0.80	0.06	0.96	0.05				
Typic	C3	0.87	0.13	0.98	0.074	0.75	0.10	0.94	0.03	0.99	0.02	0.97	0.02	0.84	0.30	0.98	0.03	0.84	0.30	0.98	0.03				
	D3	0.92	0.09	0.99	0.02	0.81	0.10	0.98	0.01	0.95	0.05	0.99	0.008	0.91	0.20	0.99	0.10	0.91	0.20	0.99	0.10				
	E3	0.90	0.09	0.99	0.01	0.78	0.09	0.98	0.01	0.99	0.02	0.97	0.01	0.91	0.22	0.99	0.13	0.91	0.22	0.99	0.13				

\*A=non-treated 200g soils.B=200g soils treated with 200ml fulvic acid (F.A.).C=200g soils treated with 0.5g monocalcium phosphate (MCP). D=200g soils treated with 200ml F.A. + 0.5g MCP. E= 0.5g MCP incorporated with 200g soils then treated with 200ml F.A.



the sandy fertilized soil takes a reverse trend. In  $D_1$  treatment, the  $b_1$  value was 0.35 against 0.25 for sandy soil fertilized with P only ( $C_1$  treatment), the corresponding value is 0.32 mg P kg<sup>-1</sup> soil in treatment  $E_1$ .

Although the same trend was also observed in alluvial and calcareous soils, the intensity factor values of uncoated P-fertilized soils ( $C_i$  treatments), are higher than those of coated P-fertilized soils ( $D_i$  and  $E_i$  treatments). However, a reverse trend was observed in capacity factors of these treatments. The capacity or the intensity values of these factors in alluvial and calcareous soils are higher than those of sandy soil treatments. Generally, from those values of P-treated soils, coating soils with fulvic acid, led to decrease soil-P bioavailability. In other words, (FA) treatment in Super-P treated soils system works as a chemical inhibitor and led to make the FA-fertilizer/soil system seems to be a slow release fertilizer.

Supplying power values of the studied soils represented by the intercept of two sites equation are shown in Table (5). The obtained results indicate that for the entire reaction period, alluvial clay soil can be able to supply P to cultivated media greater than the other soil types since  $k_2$  values are higher than those of calcareous and sandy soils. Moreover, the supplying powers of FA-treated soils were almost emphasized over the uncoated P-treated soils regardless the soil type. Data in Table (5) show also that  $k_1$  values ranged between 1.66-1.12, 1.48-1.11 and 1.16-0.42 in alluvial, calcareous and sandy soils respectively. In alluvial clay soil, FA treatment ( $E_3$ ) value was almost higher than that of  $C_2$  (alluvial treated with SP), the corresponding values of these treatments are 1.66 against 1.58, respectively. This result may related to the role of FA treatments for increasing the supplying power of the treated soil since it works as a chelating agent or a sink of P- fertilizer in soil. The same trend was almost observed in calcareous soil.

The intensity factor of P release in alluvial clay soils  $k_2$  indicates that uncoated soil has a higher ability to desorb phosphate than the coated soils. The obtained values are 0.69 and 0.55 against 1.10 in both coated and uncoated soils, respectively. This result was not observed in calcareous and sandy soils. The corresponding values are 0.35, 0.36 against 0.29 and 0.85, 0.92 against 0.80 in *Typic calcids* and *Typic psamments*, respectively. Sparks (1998), reported that type of soil component can drastically affect the reaction rate. For example, sorption reactions are often more rapid on clay minerals. This is, in large part due to availability of sites for sorption. For example, alluvial clay soil has readily available planner external and internal sites quite available for retention of sorptives than calcareous and sandy soils.

Data of modified Freundlich equation, the second fitted equation, showed that apparent desorption rate coefficient  $k_d$  was affected by fulvic acid treatments. In alluvial clay soil the  $K_d$  values decreased from 1.31 to 0.96 and 0.87 mg kg<sup>-1</sup> min in C and D treatment. The same trend was observed in both calcareous and sandy soils. In this paper, the obtained results revealed that Fulvic acid (FA) treatment worked as a slow release reactor with the studied fertilizer ions. In (E) treatment, phosphate ions adsorbed on soil particles and then coated with FA. The output of this reaction indicates that P ions were exposed to double reaction forces, the 1<sup>st</sup> was the adsorption

reaction of P ions on soil particles and the 2<sup>nd</sup> one was the chelation reaction. These two reaction forces decreased the rate of P desorption or  $k_d$  values and hence P availability in all soils. However, in FA-P treatment the obtained results show that P ions were exposed to almost only chelation force. This force permits to more release of P ions in soil system. This result could be indicted through an increase of  $K_d$  value of this treatment as compared with the above named treatment. The supposed two types of reactions are depicted in Fig. (3).

## II. Dividing the entire reaction time

Data in table ( 6 ) show the effect of dividing the entire reaction time on the rate constants of the best kinetic equations applied to describe P-release from the studied soils as affected by FA treatment i.e two sites and modified Freundlich equations. According to the two sites equation, dividing the entire reaction time into two periods showed that  $R^2$  values were almost increased in all treatments and in all soils as well (Table 5). Moreover, data in the same table indicate that dividing the entire reaction time led to a decreasing order of SE values regardless the soil types and the treatments.

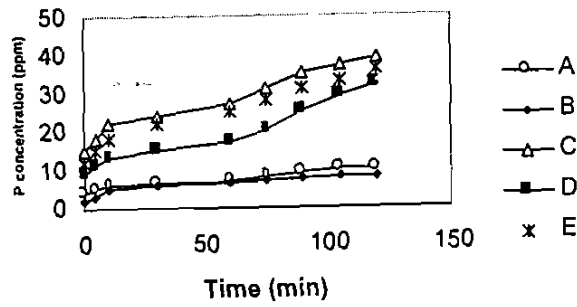
Concerning the kinetic parameters, data in Table (6) showed that the slope values represent the rate of P release of two sites equation,  $k_1$  constant, was higher in the first period (1-60 min) than in second one (60-120 min) in both  $A_3$ ,  $B_3$  and  $C_3$  as compared with  $D_3$  and  $E_3$ . A reverse trend, however was observed in intensity factor. In alluvial clay soil, the obtained values are (1.65, 0.77), (1.70, 0.73) against (0.44, 0.88) in  $E_3$ ,  $D_3$  and  $C_3$  for the first and second period respectively. This result may be due to  $H_2PO_4^-$  /  $HPO_4^{2-}$ -fulvic acid combination which decreased the P desorption in the short period of interaction of the alluvial clay soil system and a reverse trend in uncoated soil  $C_3$ . Moreover, data in the same table show that supplying power or the intensity factor values of the same soil represented by the intercept of two sites equation ( $k_2$ ) gave the same trend of increasing the first period (0-60 min) compared with the second one (60-120 min). The values of  $k_2$  were increased from 0.58 and 0.45 to 0.98 and 0.80 in  $D_3$  and  $E_3$  in the second and first period respectively. The same constant was decreased from 1.13 to 0.86 in  $C_3$ . This result indicates that phosphate-fulvic/acid system works as a slow release system. The same trend was almost observed in calcareous and for less conforming in sandy soils for the wide difference in different soil properties.

In modified Freundlich equation, data represent the apparent desorption rate coefficient  $k_d$ , and the dividing of entire reaction time (2 hrs) into two periods. Data showed that in alluvial clay soil  $k_d$  constant values are higher in the 1<sup>st</sup> period (1-60 min) than in the second one (60-120min), except in the  $C_1$  treatment. For example, the  $k_d$  values are 0.49, 0.32, 0.32, 0.89 and 0.99 against 0.25, 0.19, 0.74, 0.38 and 0.33  $mg\ kg^{-1}\ min^{-1}$ . The same trend was observed for the calcareous soil. although no obvious trend was observed in sandy soil treatments, the data indicate that incorporation of FA with P in both D and E treatment lead to minimize P release from the studied soil. in other wards, FA improves the broken properties of sandy soil and led to be worked as buffering material of P desorption from the soil.

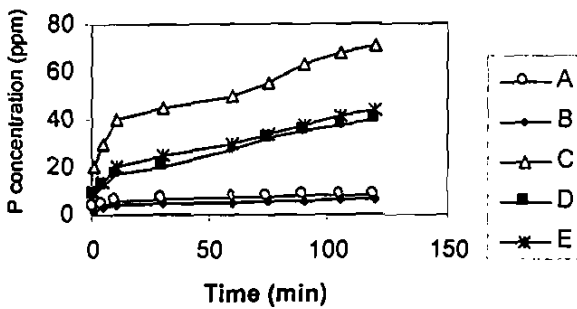
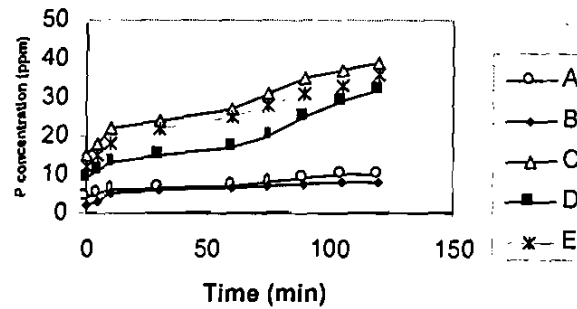
Table (6): Rate constants of selected equations that describe P-release from the studied soils at different reaction periods

Soil	Treat	Zero-order equation				1 <sup>st</sup> Order equation				M. Freundlich equation				Two sites equ			
		1 <sup>st</sup> .period	2 <sup>nd</sup> .Period	1 <sup>st</sup> .period	2 <sup>nd</sup> .Period	1 <sup>st</sup> .period	2 <sup>nd</sup> .Period	1 <sup>st</sup> .period	2 <sup>nd</sup> .Period	1 <sup>st</sup> .period	2 <sup>nd</sup> .Period	1 <sup>st</sup> .period	2 <sup>nd</sup> .Period	1 <sup>st</sup> .period	2 <sup>nd</sup> .period		
Typic	A1	0.39	0.24	0.20	0.04	0.89	5.00	0.69	1.00	0.49	0.22	0.25	0.34	0.48	0.33		
	B1	0.09	0.08	0.11	0.05	1.05	5.20	0.91	2.10	0.32	0.22	0.19	0.50	0.24	0.16		
	C1	0.91	0.81	0.85	0.76	0.05	5.20	0.05	2.70	0.32	0.23	0.74	0.54	1.88	1.20		
Psam	D1	0.35	0.63	0.42	0.49	0.46	7.90	0.22	3.10	0.89	0.31	0.38	0.60	0.67	0.78		
	E1	0.43	0.60	0.16	0.76	0.37	6.90	0.27	4.10	0.99	0.28	0.33	0.82	0.66	0.69		
	A2	0.16	0.08	0.12	0.11	0.81	3.30	0.79	2.90	0.61	0.14	0.32	0.66	0.12	0.05		
Typic	B2	0.09	0.13	0.16	0.05	0.64	1.50	0.76	1.50	0.31	0.30	0.25	0.32	0.18	0.08		
	C2	0.56	0.34	0.55	0.39	0.25	3.50	0.20	2.60	1.16	0.15	0.46	0.55	0.38	0.19		
	D2	0.34	0.33	0.50	0.40	0.47	4.10	0.51	4.40	0.94	0.16	0.69	1.07	0.20	0.12		
Cacid	E2	0.46	0.39	0.46	0.51	0.34	4.70	0.24	2.60	1.07	0.18	0.42	0.65	0.40	0.21		
	A3	0.24	0.33	0.39	0.18	0.61	6.70	0.37	2.00	0.26	0.27	0.35	0.39	1.02	0.28		
	B3	0.18	0.23	0.12	0.27	0.76	6.60	0.62	3.80	0.60	0.27	0.30	0.78	1.04	0.17		
Typic	C3	0.51	0.70	0.55	0.92	0.29	6.60	0.21	4.70	1.06	0.28	0.18	0.97	0.88	0.86		
	D3	0.39	0.69	0.50	0.96	0.40	7.80	0.16	3.10	0.43	0.61	0.96	0.30	0.73	0.80		
	E3	0.47	0.71	0.52	1.06	0.33	7.10	0.13	3.30	0.13	0.79	1.03	0.29	0.77	0.98		
Torrt																	

Alluvial Clay Soil



Calcareous Soil



Sandy Soil

Fig (1): Effect of Fulvic Acid treatments on Phosphate release from the studied soil samples

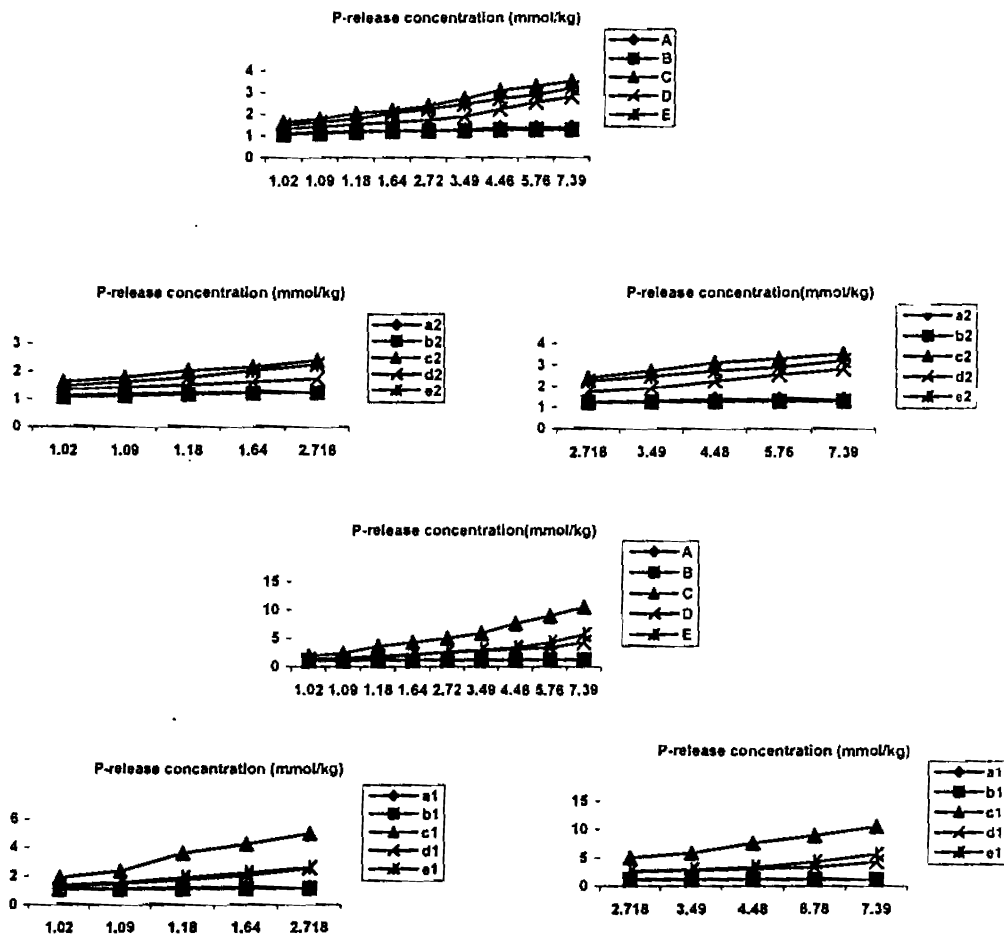
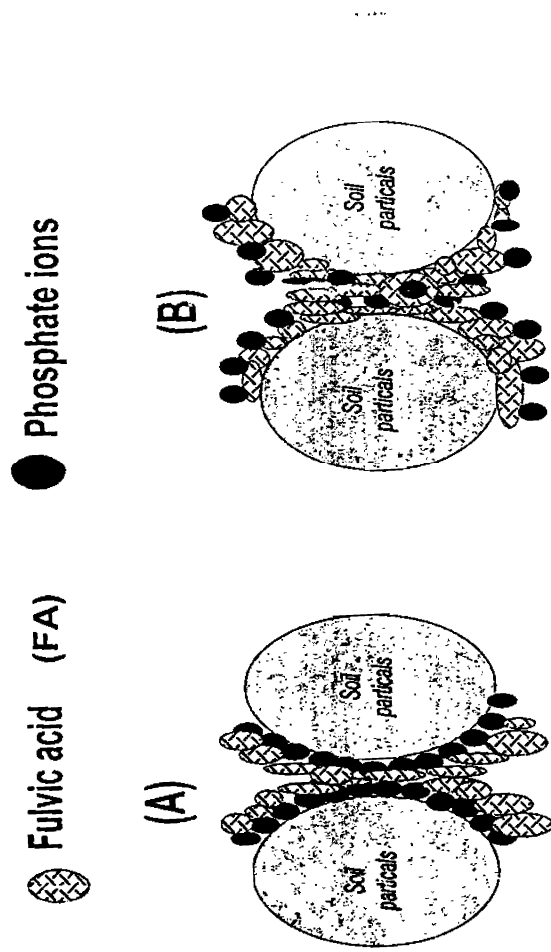


Fig.(2) : Kinetics of phosphate release from the studied soils samples expressed by Exponential and modified Freundlich equations in both entire reaction time and (a) 1<sup>st</sup>. period or (b) 2<sup>nd</sup> period.



**Fig(3)** Supposed reaction between Phosphate ions and FA representing Treatments A and (B)

The initial release rate coefficient  $b_1$  for the FA treated soils (D and E treatments) were observed to be higher in the first period compared with the second one in alluvial clay soil. This result may proven an interaction between FA as an organic material which can be worked as a slow release material and phosphate fertilizer in one side and this mixture with clay particles in other side. The inverse results of sandy and calcareous soils may be due to the effect of soil properties on availability of the initial concentration of P release.

## REFERENCES

- Abou Seeda, M.A. (1987) : Chemical and environmental aspects of sewage sludge application on Egyptian soils. Ph. D. Thesis state Univ. Gent., Gent., Belgium.
- Aharoni, C.; Sparks, D. L.; Levinson, S, and Ravina, I. (1991) Kinetics of soil chemical reactions: Relationships between empirical equations and diffusion models. *Soil Sci. Soc. Am. J.* 55:1307-1312.
- Amer, F., Bouldin, D.R., and Black, C.A. (1955). Characterization of soil phosphorus by anion exchange resin adsorption and  $P^{32}$  equilibration . *Plant and soil* 6: 391-394.
- Barrow, N. J., and Shaw, T. C. (1975) The slow reaction between soils and anions . 5. Effect of period of prior contact on the soil desorption of phosphate from soils. *Soil Sci.* , 119: 311-320.
- Cooke, I.J.(1966): A kinetic approach to the description of soil phosphate status. *J. soil. Sci.* 17: 56-64.
- Cottenie, A. ; Verlea, M. ; Krekens, L. ; Velghe, G., and Bcamerlynck, R. (1982). Chemical analysis of plant and soils Lab. Anal. Agroch. Fac. Agric. State University Gent., Belgium.
- Elkhatib, E. A., and Hern, J. L. (1988). Kinetics of phosphorus desorption from Appalachian soils. *Soil Sci.* , 145 : 222 - 229 .
- Evan, R. L., and Jurinak, J. J. (1976) . Kinetics of phosphate release from a desert soil. *Soil Sci.*, 121: 205 - 211.
- Havlin, J. L. , and Westfall, D. G. (1985). Potassium release kinetics and plant response in calcareous soils. *Soil Sci. Soc. Am. J.* , 49: 366 - 370
- Kuo, S., and Lotse, E.G. (1972) : Kinetics of phosphate adsorption kinetics and its relationship with plant growth. *Soil. Sci. Soc. Am. J.* 58: 416-423.
- Raven, K. P., and Hossner, L. R. (1994) . Soil phosphorus desorption kinetics and its relationship with plant growth. *Soil Sci. Soc. Am. J.* , 58 : 416 - 423 .
- Sharply, A. N., and Ahuja , L. R. (1982) . Effects of temperature and soil - water content during incubation on the desorption of phosphorus from soil . *Soil Sci.* , 6 : 350 - 355 .
- Sparks, D. L. (1987) Kinetics of soil chemical processes : Past progress and future Needs." *Soil Sci. Soc. Am.*, Madison, Wisconsin.

- Sparks, D. L. (1989). Kinetics of soil chemical processes. Academic Press, San Diego, CA.
- Sparks, D. L. (1998). Soil Physical Chemistry, Second Edition, Lewis publishers, CRC press, London.
- Sayin, M. ; Mermut, A. R., and Tiessen, H. (1990). Phosphate sorption - desorption characteristics by magnetically separated soil fractions. Soil Sci. Soc. Am. J. , 54 : 1298 - 1304 .
- Zaghloul, A.M. (1998) Kinetics of phosphate releases in some soils of Egypt. Ph.D. Thesis, Soil Dept., Faculty of Agriculture, Ain Shams Univ. Egypt.
- Zaghloul, A.M. and El-Ashry, S.M. (2000) Kinetics of potassium adsorption in some soils of Egypt using Electrical Stirred Flow Unit (ESFU). Congress of "SOIL AND SUSTAINABLE AGRICULTURE IN THE NEW CENTURY" October 23-25, 2000, Cairo, Egypt.

### تقييم الصورة المنطلقة لعنصر الفوسفور في بعض الأراضي المصرية المعاملة بحامض الفولفيك

- علاء زغلول\* ، محمد على طه أبو سعدة\*\* و هشام إبراهيم العيلة\*\*
- \* قسم الأراضي واستغلال المياه- المركز القومي للبحوث - الدقى - الجيزة
- \*\* قسم تغذية النبات - المركز القومي للبحوث - الدقى - الجيزة -

تلعب المادة العضوية دوراً هاماً في زيادة معدل تيسر العناصر الغذائية في الأراضي كما أنها في بعض الأحيان تزيد من القدرة الإمصاصة لبعض الأراضي الرملية ولذلك أجريت تجربة معملية لتقييم دور الأحماض العضوية الذاتية (حامض فولفيك سيد FA) بعدة طرق على انطلاق عنصر الفوسفور من خلال دراسة كينيتيكية لعنصر الفوسفور المنطلق حيث تشير النتائج الآتى :

- أثبتت معادلة Freundlich (First order, Two sites) كفاءة عالية في وصف معدل انطلاق عنصر الفوسفور في الأراضي الرملية حيث أعطت أعلى قيم لإنتلاق هذا العنصر وذلك إذا ما قورن ببقاى الأراضي تحت الدراسة.
- كما أظهرت النتائج أيضاً أن إضافة حمض الفولفيك قد أدت إلى انخفاض معدل انطلاق الفوسفور خاصة في الأراضي الطينية مما يؤدي إلى زيادة زمن التفاعل الكلى لإنتلاق هذا العنصر خلال مراحل نمو النبات.
- أوضحت النتائج أيضاً أن القدرة الإمدادية للأراضي المعاملة بحامض الفولفيك كانت أفضل في زيادة إمداد عنصر الفوسفور إذا ما قورنت بالأراضي غير المعاملة مما يؤكد أهمية الدور الذى تلعبه الأحماض العضوية الذاتية (FA) في زيادة القدرة الإمدادية نتيجة للدور المخلبى الذى تقوم به المادة العضوية.