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Kinetics of Phosphate Adsorption As Affected by Vertisols Properties

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THE STUDY of phosphate sorption by soils and clay minerals has particular interest, but little is known about the quantitative importance of phosphate sorption by vertisols and soil properties affecting it. The kinetic of phosphate adsorption was investigated by using three sources of phosphatic fertilizers, namely: potassium dihydrogen phosphate (S_1), potassium diammonium phosphate (S_2), and potassium poly phosphate (S_3). Ten soil surface alluvial clay samples (*Typic Torrerts*) different in their characteristics, and pure clay minerals as montmorillonite, illite, and kaolinite were used in these experiments to the kinetic study applied for the entire reaction time ranging between 1 to 120 min. Phosphate sorption data was fitted to both empirical models (modified Freundlich and Elovich equations) and theoretical ones (first-order and apparent diffusion equations). Calculating the phosphorus sorption index (PSI) for the studied three clay minerals were estimated according to coefficient of determination (R^2). Results show that Elovich equation is the best fitted equation could describe the kinetic data in both alluvial clay soils and clay minerals. Also, potassium diammonium phosphate (S_2) is superlative source to be applied in vertisols compared to other sources applied in this study, since it has the higher values in most kinetic parameters of tested models *i.e.* modified Freundlich (K_{ad}, b\), Elovich (α , β), Parabolic diffusion (R, b) and first order (k, v). The statistical analyses show that kinetic parameters of tested equations were highly correlated with each of clay content, specific surface area, available P, total and amorphous iron, manganese and aluminum, some soil parameters. The same trend of results was found for various sources of P applied but with different degrees of significance correlation. The highest value of PSI (286.04 mg/L) was noted in S2-montmorillonite system and the lowest one was obtained in S_1-kaolinite system (196.67 mg/L). According to the kinetic and PSI parameters for different sources adsorbed on vertisols or intensity and capacity factors of P-bioavailability in soils, they can take the following descending order:potassium diammonium phosphate (S_2)> potassium polyphosphate (S_3)>potassium dihydrogen phosphate (S_1) .

Keywords: Vertisols, Montmorillonite, Illite, Kaolinite.

Adsorption and desorption are the most important soil processes governing phosphorus concentration in soil solution The availability of the applied P is controlled by adsorption and desorption characteristics of the soil. The main soil properties that influence these reactions include the amount and the type of clay, amount of iron and aluminum oxides, organic matter content, pH and calcium carbonate content (Solis and Torrent, 1989 and Wahba, 1991).

The study of phosphate adsorption on soil has a particular interest, but limited information is known about the quantitative importance of phosphate adsorption by vertisols and the most soil properties affecting this chemical process. Little laboratory time and work needed to produce adsorption curve, but for basic recommendation purposes, it is more practical to have a knowledge of which soil properties of those usually determined on a routine basis are correlated with adsorption parameters. This correlation changes from one group of soils to another according to the type and concentration of soil constituents affecting P adsorption. In Vertisols and vertic subgroups of other soil orders limited information is known regarding which soil properties are related to P adsorption Extractable Fe, clay content, extractable Al and organic matter content are some of those soil parameters affecting P adsorption/ characteristics (Singer,1978; Burtham and Lopez Heinandez,1982; Nychas and Kosmas, 1984). In this respect, another researchers found that the main components involved in P-adsorption and surface charge are types and the amounts of dominant clay minerals, various oxides (Barron *et al.*, 1988; Bigham *et al.*, 1978; Hue, 1991; Moshi *et al.*, 1974 and Wahba, 1991). Accordingly, some significant relationships have been found among P-adsorption capacity, surface charge and soil properties. Such properties may include texture, colour, and the amounts of soluble Fe and Al dissolved in some reagents and other minerals.

The current work is mainly devoted to study : (I) the kinetics of phosphate adsorption on vertisols as affected by the source of P-fertilizer added and the soil properties, (II) elucidate the nature of phosphate from these fertilizers on clay minerals using an array of kinetic models representing both empirical and theoretical types of equations, and (III) to declare the most soil properties affecting P adsorption through the correlation analysis between the kinetic parameters of different kinetic models and the various properties of the studied soils.

Material and Methods

Ten alluvial soil surface samples (0-50 cm) different in their properties, were collected from Menofia Governorate representing Typic Torrerts according to Soil Survey Staff (1998). Soil samples were air dried and passed through a 2 mm sieve. The soil samples were analyzed for particle size distribution, pH , total soluble salts, total and active $CaCO_3$, organic matter content, available P and cation exchange capacity using standard methods (Black *et al.*, 1 982).

Surface area was measured by the method of Lawrie (1961) which is a rapid method for determination of approximate surface area of soil by calculating the adsorbed molecules of O- phenanthroline according to the following equation :

$$A = M \times 3.61 \text{ m2/g of soil}$$

Where : M = the amount of O-phemanthroline in millimols per 100g soil .

Amorphous iron and aluminum extracted by dithionite citrate-bicarbonate (DCB) buffer solution according to Black *et al.* 1982 , Fe and Al were determined by atomic adsorption equipment.

Adsorption determination of the studied Vertisols

In batch technique, exactly 5 gm of each soil sample was put in plastic centrifuge tubes and 50 ml solution of each diammonium phosphate, polyphosphate and potassium dihydrogen phosphate fertilizers previously prepared at 90 ppm P concentration was added.

The tubes were vigorously shacked using end-over end shaker for various times: 1,5,10,30,60,75,90,105 and 120 min. At the end of each time the tubes were centrifuged, filtered and the supernatant were analyzed for their P concentrations. The amount of P adsorbed was obtained by subtracting P concentration in the beginning of the experiment (q_o) from phosphate concentrations in each pure solution samples (qt) at a given time of reaction, this difference representing the kinetics of P adsorption for different sources of P-fertilizers on different soil samples.

Kinetics of phosphate adsorption on clay minerals as affected by source of P-fertilizers

Pure specimens of kaolinite, illite, and montmorillonite (clay mineral standard of Ward's Natural Science Establishment) were applied as follows: 100 mg of each mineral were placed in 100 ml plastic bottles and aliquots of 5 ml containing 90 ppm P of each fertilizers previously mentioned. A few drops of toluene were added to inhibit microbial growth. The suspension was shaken for the abovmentioned periods applying in adsorption study at room temperature. At the end of each reaction time, the tubes were centrifuged for 10 min at 7000 rpm and directly filtered. The amount of P sorbed was calculated by the same way previously mentioned in kinetic study. Phosphorus was colormetrically determined by using ascorbic acid method of Murphy and Riley (1962).

Kinetic equations

Using regression analysis, the P adsorption data were fitted, to both empirical equations *i.e* modified Freundlich (power function) in the form ($q - K_{ad}\, t b^{\backslash}$), and Elovich, ($q = 1/\beta \ln \alpha\beta + 1/\beta \ln t$) and theoretical equations *i.e.* parabolic diffusion ($q = b + R\, t^{0.5}$) and first-order kinetic equations $q = \log v - kt$.

Where

q = the amount of phosphate adsorbed in time t
k_{ad} = adsorption rate coefficient in mg kg^{-1} soil min^{-1}
$b^{\backslash}$ = intensity constant in mg P kg^{-1} soil
β = a constant related to the initial rate of P adsorbed in mg P kg^{-1} min^{-1}

α = a constant in mg kg^{-1} soil
b = intensity constant in mg P kg^{-1} soil
R = the apparent diffusion rate coefficient in mg P kg^{-1} soil min^{-1}
v - the maximum amount of P adsorbed mg P kg^{-1} soil
k= the rate constant of the reaction in min^{-1}

the best fitted equation (s) was judged by the higher coefficient of determination (R^2). Phosphate Sorption Index (PSI) was also determined by applying the equation :

$$PSI = X/\log C$$

where:
X= the amount of P adsorbed in mg P/kg soil
C= equilibrium P concentration in μg P/L

Results and Discussion

Soil properties: Particle size distribution of the studied vertisols samples indicate that all samples have high content of clay (50.30 to 63.21%). Data of the chemical analysis indicate alkalinity trend and high values of specific surface area (208 to 316 m2/g) due to the high amount of clay, relatively high content of available phosphorus. Also total iron, amorphous Fe, Al and Mn are high (Table 10). Wahba (1991) found that a significant (at 0.01 level) positive correlation between each of Fe and Mn and clay (r = 0.86 , 0.88) silt (r = 0.61 , 0.59). Manganese mostly associated with clay content, pH, organic matter and redox conditions in soil.

Results presented in Table 2 show the regression equations of four different kinetic equations that describe phosphate adsorption from clayey soil (*Typic Torrerts*) from 1-120 min with potassium dihydrogen phosphate (S_1) , diammonium phosphate (S_2) and potassium poly phosphate (S_3), calculated as mg P /kg. The mean of R^2 values were in the order: Elovich >modified Freundlich>parabolich diffusion> first-order. These results coincide with Chien *et al.* (1980) who found that Elovich equation was the best fitted equation to describe phosphate release and sorption for the experimental data. The equation successfully describes the data as a single straight line that covers the entire course of reaction time . It also show that constants α and β may be used for comparing the reaction rates of phosphate release or sorption in different soils . In this respect Sikora *et al* (1991) suggested that the Elovich α constant may be a useful parameter to predict P availability in soils and fertilizer materials if the P-dissolution rate is proven to be the limiting for uptake by roots. The modified Freundlich equation in the linear form is $\ln ct = \ln k_{ad} + b' \ln t$. The integrated form is $qt = k_{ad}\, tb`$ where qt is the amount of P adsorbed at time t , $k_{ad}$ and b are constants . Taking the derivation of integrated form: $dq / dt\ \ k_{ad}\, b`t^{\,b-1}$ where kd is directly proportional to the rate of P adsorbed and was considered as the apparent desorption rate coefficient. The effect at b` on phosphate adsorbed is more complex . The reaction rate is proportional to kad only at t  1 in which case : $dq / dt\ \ k_{ad}\, b`$. The b` value is convenient to use as estimate of the initial P adsorbed rate when comparisons are made between modified Freundlich equations. It is however, designated the reversibly adsorbed phosphate.

Table 3 shows that both the apparent coefficient rate of phosphate adsorption (k_{ad}) and the reversibly adsorbed phosphate (b`) consistently increase with fertilizer $S_2 > S_3 > S_1$ respectively . In the same table the constant values of Elovich kinetic equation describing phosphate adsorbed from soil are estimated . The equation was applied in simple modified linear form $q = 1/\beta \ln \alpha + 1/\beta \ln t$. Chien and Clayton (1979) showed that the decrease in β and or increase in α enhance the reaction rate . The trend of 1/β followed that of k_{ad} in modified Freundlich equation as affected by the source of fertilizer added and the time different . With regard to the relationship between β constant values and the type of added fertilizer phosphate , the presented data in Table 3 indicated that β, α P- intensity values were the highest with S_2 fertilizer compared with S_3 and S_1 respectively in all soils . The rate of phosphate adsorbed was studied through the determination of the diffusion rate coefficient R and parameter b which is presumably the quantity of phosphate in solution at time = 1 (Moser *et al* ., 1959) the slope and the intercept of data according to parabolic diffusion equation in the form: $q = b + Rt^{0.5}$ where q = the amount of P adsorbed in the time, R=apparent diffusion rate coefficient and b = intensity factor. The kinetic parameters R and b are presented for the clay soil fertilized with S_1 , S_2 , S_3 with different times . In Table 3 the figures indicate that both the rate of phosphorus adsorption R and the intensity factor b consistently increased with S_2 than S_3 and S_1 respectively in all soil samples . The kinetic parameters of the first order equation (the rate constant

TABLE 1. Some chemical characteristics of the soil samples used .

Sample N°	Total $CaCO_3$ %	Active $CaCO_3$ %	O . M %	Surface Area m^2/g	Available P ppm	Total Fe %	Am.Fe_2O_3 ppm	Am. Mn_2O_3 ppm	Am. Al_2O_3 ppm
1	7.65	3.30	2.68	316	425.56	5.7	28560	130.2	204.5
2	7.95	3.71	2.66	291	404.49	5.5	35670	150.3	224.4
3	7.20	3.16	1.50	257	328.65	5.4	32510	146.4	216.3
4	8.25	3.85	1.44	241	286.52	5.3	30501	1422	212.7
5	7.50	2.89	1.63	235	282.30	5.2	40880	153.5	232.3
6	7.95	3.30	1.47	233	278.09	5.0	45720	170.1	237.9
7	7.50	2.61	1.65	232	248.56	4.8	42940	158.3	233.8
8	8.70	3.58	1.96	231	240.17	4.7	46380	180.2	249.1
9	7.05	3.16	2.01	230	206.46	4.4	47180	185.1	265.5
10	8.10	3.03	1.52	208	198.03	3.9	25034	120.4	114.6

Am = Amorphous

TABLE 2. Regression equations and coefficient of determination (R^2) values for phosphate adsorption from different sources of phosphate fertilizers.

N°	Equation Type	Potassium dihydrogen phosphate		Diammonium phosphate		Potassium poly phosphate	
		Equation	R^2	equation	R^2	equation	R^2
1	Modified Freundlich	$y = 30.0\ t + 39$	0.88	$y = 50.4t+47.86$	0.97	$y = 37.6t+43.1$	0.85
	Elovich	$y = 0.38t+50.5$	0.83	$y = 2.5t+70.62$	0.95	$y=2.41t+59.18$	0.84
	Parabolic Diffusion	$y=0.27t+55.5$	0.95	$y=1.07t+76.39$	0.85	$y=1.04t+57.35$	0.96
	First-order	$y=9.29t+1.06$	0.83	$y=12.3t+1.73$	0.91	$y=11.1+1.39$	0.85
2	Modified Freundlich	$y=32.3t+39$	0.88	$y=51.9t+60.26$	0.97	$y=42.7t+50.7$	0.86
	Elovich	$y=0.68t+5.6$	0.86	$y=3.26t+65.89$	0.89	$y=2.63t+54.7$	0.94
	Parabolic Diffusion	$y=0.35t+54.8$	0.97	$y=1.50t+69.1$	0.82	$y=1.21t+67.36$	0.70
	First-order	$y=7.3t+0.94$	0.92	$y=10.6t+1.69$	0.85	$y=10.2t+1.48$	0.99

TABLE 2 . cont.

N°	Equation Type	Potassium dihydrogen phosphate		Diammonium phosphate		Potassium poly phosphate	
		Equation	R^2	equation	R^2	equation	R^2
3	**Modified Freundlich**	$y =31.3t+41.2$	0.94	$y =51.2t+58.88$	0.98	$y =42.6t+48.98$	0.83
	Elovich	$y =0.54t+53.4$	0.92	$y =3.13t+67.50$	0.96	$y=2.62t+55.70$	0.79
	Parabolic Diffusion	$y=0.30t+54$	0.96	$y=1.33t+70.48$	0.95	$y=1.17t+55.92$	0.94
	First-order	$y=7.4t+0.71$	0.92	$y=10.7t+1.70$	0.85	$y=10.7t+1.08$	0.95
4	**Modified Freundlich**	$y =30.5t+40$	0.98	$y=51.1t+56.57$	0.84	$y=38.9t+44.88$	0.85
	Elovich	$y =0.46t+52.5$	095	$y=2.87t+70.29$	0.97	$y=2.45t+57.77$	0.91
	Parabolic Diffusion	$y =0.28t+56$	0.98	$y=1.27t+71.38$	0.86	$y=1.15t+56.34$	0.98
	First-order	$y =7.6t+0.67$	0.96	$y=11.55t+1.50$	0.94	$y=11.0t+1.29$	0.90
5	**Modified Freundlich**	$Y=37.5t+47.5$	0.89	$y=61.0t+61.66$	0.96	$y=53.2t+52.23$	0.94
	Elovich	$Y=0.7t+55.8$	0.91	$y=3.29t+47.77$	0.87	$y=2.67t+64.8$	0.92
	Parabolic Diffusion	$Y=0.37t+55.4$	0.99	$y=1.54t+68.77$	0.99	$y=1.23t+66.55$	0.70
	First-order	$Y=6.4t+0.94$	0.93	$y=10.5t+1.88$	0.91	$y=10.1t+1.34$	0.70
6	**Modified Freundlich**	$y=42.5t+54.29$	0.98	$y=67.2t+66.07$	0.95	$y=59.7t+57.01$	0.96
	Elovich	$y=0.85t+47.57$	0.88	$y=3.91t+67.57$	0.98	$y=2.78t+59.01$	0.93
	Parabolic Diffusion	$y=0.40t+57.3$	0.95	$y=1.96t+65.63$	0.91	$y=1.42t+58.63$	0.91
	First-order	$y=5.3t+0.58$	0.96	$y=9.8t+1.50$	0.94	$y=9.1t+1.19$	0.90

TABLE 2 . cont.

N^0	Equation Type	Potassium dihydrogen phosphate		Diammonium phosphate		Potassium polyphosphate	
		Equation	R^2	equation	R^2	equation	R^2
7	Modified Freundlich	$y=38.5t+53.70$	0.93	$y=65.9t64.56$	0.98	$y=59.5t+54.90$	0.98
	Elovich	$y=0.75t+49.50$	0.96	$y=3.51t+70.67$	0.99	$y=2.77t+58.3$	0.96
	Parabolic Diffusion	$y=0.39t+56.7$	0.83	$y=1.81t+66.23$	0.94	$y=1.30t+60.05$	0.97
	First-order	$y=5.9t+1.10$	0.82	$y=9.9t+1.63$	0.96	$y=9.15t+1.33$	0.94
8	Modified Freundlich	$y=49t+57.5$	0.89	$y=69.9t+67.61$	0.96	$y=61t+56.70$	0.90
	Elovich	$y=0.89t+53.68$	0.92	$y=4.53t+63.28$	0.87	$y=3.26t+59.05$	0.93
	Parabolic Diffusion	$y=0.57t+54.13$	0.99	$y=2.02t+64.14$	0.82	$y=1.4t+58.13$	0.98
	First-order	$y=5.2t+0.53$	0.92	$y=9.7t+1.17$	0.94	$y=8.9t+0.97$	0.89
9	Modified Freundlich	$y=52.5t+61.3$	0.73	$y=74.9t+69.18$	0.96	$y=62.5t+63.0$	0.96
	Elovich	$y=1.22t+51.37$	0.95	$y=5.18t+66.40$	0.96	$y=3.78t+61.70$	0.96
	Parabolic Diffusion	$y=63t+53.14$	0.99	$y=2.3t+63.23$	0.84	$y=1.64t+59.80$	0.93
	First-order	$y=5.0t+0.5$	0.96	$y=7.4t+1.19$	0.87	$y=6.1t+0.69$	0.94
10	Modified Freundlich	$y=29.3t+38.3$	0.89	$y=42.2t+47.00$	0.96	$y=37.5t+41.5$	0.91
	Elovich	$y=0.34t+50.0$	0.91	$y=2.15t+70.61$	0.99	$y=2.15t+63.58$	0.94
	Parabolic Diffusion	$y=0.25t+51.1$	0.98	$y=1.03t+77.71$	0.90	$y=0.87t+64.61$	0.98
	First-order	$y=9.3t+1.19$	0.95	$y=13.4t+1.82$	0.96	$y=11.12t+1.41$	0.99

of P- adsorbed K and V the intensity of P) showed patterns similar to those of the corresponding parameters of the other three kinetic equations though the K and V values were the highest with S_2 and more than S_3 and S_1 respectively in all soils.

TABLE 3 . Kinetic parameters for several equations described phosphate adsorbed from alluvial soil samples.

N°	Modified Freundlich		Elovich equation		Parabolic diffusion		Ist. order	
	K_{ad}	b\	β	α	R	b	K	V
with potussium dihydrogen phosphate .								
1	30.0	39.0	0.38	50.5	0.27	55.0	9.29	1.06
2	32.3	45.0	0.68	50.6	0.35	54.8	7.30	0.94
3	31.3	41.2	0.54	53.4	0.30	54.0	7.40	0.71
4	30.5	40.0	0.46	52.5	0.28	56.0	7.60	0.67
5	37.5	47.5	0.70	55.8	0.37	55.4	6.40	0.94
6	42.5	54.29	0.85	47.57	0.40	57.3	5.30	0.58
7	38.5	53.70	0.75	49.50	0.39	56.7	5.9	1.10
8	49.0	57.5	0.89	53.68	0.57	54.13	5.2	0.53
9	52.5	61.3	1.22	51.37	0.63	53.14	5.0	0.50
10	29.3	38.3	0.34	50.0	0.25	51.1	9.3	1.19
With diammonium phosphate .								
1	50.4	47.86	2.50	70.62	1.07	76.39	12.3	1.73
2	51.9	60.26	3.26	65.89	1.50	69.1	10.6	1.69
3	51.2	58.88	3.13	67.5	1.33	70.48	10.8	1.70
4	51.1	56.57	2.87	70.29	1.27	71.38	11.55	1.50
5	61.0	61.66	3.29	47.77	1.54	68.77	10.5	1.88
6	67.2	66.07	3.91	67.57	1.96	65.63	9.8	1.50
7	65.9	64.56	3.51	70.61	1.81	66.23	9.9	1.63
8	69.9	67.61	4.53	63.28	2.02	64.14	9.7	1.17
9	74.9	69.18	5.18	66.4	2.30	63.25	7.4	1.19
10	42.2	47.00	2.15	70.61	1.03	77.71	13.4	1.82
With potassium poly phosphate .								
1	37.6	43.1	2.41	59.18	1.04	57.35	11.1	1.39
2	42.7	50.7	2.63	54.7	1.21	67.36	10.2	1.48
3	42.6	48.98	2.62	55.6	1.17	55.92	10.7	1.08
4	38.9	48.88	2.45	57.77	1.15	56.34	11.0	1.29
5	53.2	52.23	2.67	64.8	1.23	66.55	10.1	1.34
6	59.7	57.01	2.78	59.01	1.42	58.63	9.10	1.19
7	59.5	54.90	2.77	58.3	1.30	60.05	9.15	1.33
8	61.0	56.7	3.26	59.05	1.48	58.13	8.9	0.97
9	62.5	63.0	3.78	61.70	1.64	59.80	6.1	0.69
10	37.5	41.5	2.06	63.58	0.87	64.61	11.12	1.41

For clay minerals, Sparks (1989) reported that one of the most important factors influence the rate of phosphate exchange on the soil and soil constituents is clay mineralogical composition . In this respect Abdou *et al.* (1980) concluded that the montmorillonite is the major soil mineral in the alluvial soils of Egypt with low content of kaolinite and illite. From quantitative point of view El-Araby (1973), Ibrahim (1975) and Khalil and Labib (1976) in their studies on the soils of the Northern part of the Nile Delta, recorded that the percentages of montmorillonite are 53.6 , 49.3 and 50 , and the percentages of kaolinite are 22.47, 16.22 and 14.40 respectively while the percentages of illite are 9.98, 12.8 and 12.5 respectively . The results in Table 4 indicate that all four tested equations gave highly significant R^2 according to the rule that the conformity of the adsorption data to a particular kinetic equation is judged by the higher coefficient of determination (R^2) of regression. Elovich equation showed the highest coefficient of determination (0.938) followed by the first order equation, parabolic diffusion and modified Freundlich (0.934, 0.931 and 0.874 respectively) . It is noteworthy that the Elovich equation was the highest coefficient of determination with clay minerals as well as the soil samples. However, the superiority of Elovich equation over the other used equation has also been documented by Polyzopoulos *et al.*, (1985). In the same table , the K_{ad} constant of phosphate adsorbed was considerably affected by both kind of fertilizer and type of clay mineral . It appears that the K_{da} value of the montmorillonite with (S_2) was more than K_{ad} value of montmorillonite with (S_1, S_3 respectively) . Similar trend was observed in S_2 with illite and kaolinite. It is noteworthy that the K_{ad} value of kaolinite with (S_2) was lower than K_{ad} value of montmorillonite, illite. In other words the Kad values of clay minerals 2 : 1 were more than k_{ad} values of clay minerals 1:1 as shown in Fig. 1. Table 5 showed that the intercept (b`) designated as the reversibly adsorbed phosphate , highest value b` was with (S_2) montmorillonite compared to the b` value of (S_1,S_3) with montmorillonite respectively. The β value was the highest in the fertilizer diammounim phosphate (S_2) compared to other fertilizers . The constant α was suggested to be an important parameter in defining d (P) / d (t) at low time period (Sikora *et al.* 1991).Generally the constant α increased with the type of clay mineral 2:1 since types were more than 1:1 and higher values with (S_2) than (S_1, S_3) in all cases . The values of the constants of parabolic diffusion equation , R and b as R is the diffusion rate coefficient and the parameter b which is presumably the intensity factor of P. The slope and the intercept of the data are plotted according to

TABLE 4. Regression equations and coefficient determination (R^2) values for phosphate adsorption with different sources of phosphate fertilizers on clay minerals.

mineral	Equation type	Potassium dihydrogen phosphate		Diammonium phosphate		Potassium poly phosphate	
		Equation	R^2	equation	R^2	Equation	R^2
Montmorillonite	Modified Freundlich	y=3.7t+537.03	0.87	y=4.5t+776.25	0.78	y=3.81t+724.43	0.92
	Elovich	y=20.2t+692.3	0.92	y=26.12t+778.3	0.95	y=22.47t+729.9	0.93
	Parabolic Diffusion	y=9.04t+699	0.92	y=11.73t+787	0.93	y=10.11t+737	0.94
	First-order	y=-8.2t+1.93	0.94	y=11.1t+2.10	0.91	y=-8.6t+2.0	0.95
Illite	Modified Freundlich	y=4.01t+588.8	0.90	y=6.2t+691.83	0.92	y=5.61t+601.2	0.90
	Elovich	y=19.89t+612.7	0.93	y=24.41t+687.6	0.94	y=22.13t+649.19	0.90
	Parabolic Diffusion	y=9.09t+618.7	0.95	y=11.06t+693.80	0.91	y=9.69t+656.39	0.94
	First-order	y=-7.9t+1.92	0.96	y=-9.9t+1.98	0.91	y=-8.3t+1.95	0.91
Kaolinite	Modified Freundlich	y=4.9t+389.1	0.95	y=8.2t+478.63	0.78	y=5.9t+426.6	0.86
	Elovich	y=19.14t+470	0.93	y=19.9t+591.1	0.96	y=19.40t+536	0.94
	Parabolic Diffusion	y=8.52t+478	0.96	y=9.01t+597	0.94	y=8.81t+545	0.98
	First-order	y=-6.8t+190	0.95	y=-9.01t+1.96	0.95	y=-8.2t+1.92	0.93

TABLE 5. Kinetic parameters of the applied equation described phosphate adsorbed of clay minerals with different phosphate fertilizers.

Type of clay mineral	Type of Fartilizer	Modified Freundlich		Elovich equation		Parabolic diffusion		Ist. order	
		K_{ad}	b\	β	α	R	b	K	V
Montmori-llonite	1*	3.70	537.03	20.0	692.3	9.04	699	- 8.2	1.93
	2*	4.50	776.25	26.12	778.3	11.73	787	- 11.1	2.10
	3*	3.81	724.43	22.47	729.9	10.11	737	- 8.6	2.0
Illite	1*	4.01	588.8	19.89	612.70	9.09	618.7	- 7.9	1.92
	2*	6.20	691.83	24.41	687.60	11.06	693.8	- 9.9	1.98
	3*	5.61	601.2	22.13	649.19	9.69	656.39	- 8.3	1.95
Kaolinite	1*	4.9	389.1	19.14	470.0	8.52	478	- 6.8	1.90
	2*	8.2	478.63	19.19	591.1	9.01	597	- 9.01	1.96
	3*	5.9	426.6	19.40	536.0	8.81	545	- 8.2	1.92

1* Potassium dihydrogen phosphate.

2* Diammonium phosphate.

3* Potassium polyphosphate.

parabolic diffusion for clay minerals. The R value was higher with (S_2) compared to (S_1 , S_3) respectively in all minerals and the intensity coefficient b was greatly affected by the type of fertilizer. k_{ad} the rate constant of P adsorbed and V the intensity of P showed patterns similar to those of the corresponding parameters of other three kinetic equations though changes were not very sensitive.

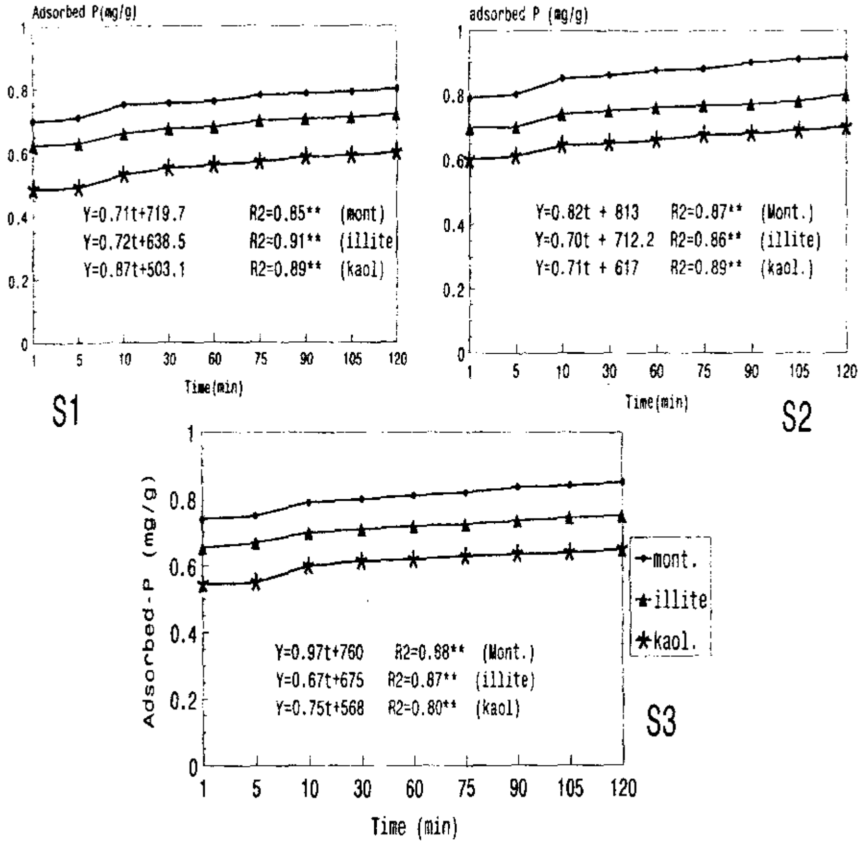

Fig. 1. Kinetics of P-adsorbed on clay minerals using different phosphatic commercial fertilizers

On the other hand , the average value for the phosphorus sorption index (PSI) of montmorillonite treated with (S_2) was higher than S_3 , S_1 (286.04 compared to 260.53 and 275.28 mg P/L respectively). The values of the phosphorus sorption index (PSI) can take the following descending order:

S_2 - montmorillonite >S_2 - illite>S_2 - kaolinite . The PSI reflects the numbers of unsatisfied P sorption according to Laverdiere and Karam (1984) . Tsadilas, Samaras and Dimoyiannis (1996) suggested that the P sorption index was strongly correlated with the clay content and less strongly with dithionite-extractable Fe and Al such as showed in Table 6, the correlation coefficient between soil properties and the constants of kinetic models that best describe phosphate adsorbed from the studied alluvial soil samples.

TABLE 6. Correlation coefficient (r) between soil properties and the constants of the kinetic models that best describe phosphate adsorbed from the studied alluvial soil samples with potassium diammonium phosphate.

Soil Properties	Freundlich		Elovich		Parabolic diffusion		Ist. order	
	K_{ad}	b\	β	α	R	b	K	V
Clay	0.91***	0.85***	0.81***	0.97***	0.86***	0.62***	-0.47**	-0.75***
Surface Area	0.96***	0.88***	0.88***	0.92***	0.98***	0.67***	-0.54**	-0.85***
Available-P	0.97***	0.92***	0.86***	0.95***	0.97***	0.59***	-0.66***	-0.86***
Amorphous – Fe	0.87***	0.94***	0.81***	0.92***	0.85***	0.54**	-0.74***	-0.75***
Amorphous- Mn	0.93***	0.94***	0.88***	0.95***	0.93***	0.66***	-0.66***	-0.84***
Amorphous- Al	0.70***	0.74***	0.69***	0.78***	0.72***	0.62***	-0.57***	-0.59***
Total-iron	0.57**	0.65***	0.76***	0.57**	0.54**	0.88***	ns	-0.72***

Conclusions

Phosphate kinetic by Vertisols from Menofia governorate and clay minerals "montmorillonite, illite, kaolinite" were treated by three sources of P fertilizers "potassium dihydrogen phosphate (S_1), diammonium phosphate (S_2), and potassium polyphosphate (S_3). The empirical models of modified Freundlich and Elovich equations and theoretical one first order and apparent diffusion equations were tested. Elovich equation was the best fitted equation which could describe the kinetic data in both alluvial clay soils and clay minerals. Potassium diammonium phosphate is superlative source to be applied in Vertisols compared to other sources of phosphate fertilizer. The statistical analysis show that kinetic parameters of tested equations were highly correlated with clay, available P, total and amorphous Fe,Mn,Al content and surface area. The highest value of PSI was noted in diammonium phosphate with montmorillonite system and the lowest one was obtained in potassium dihydrogen phosphate with kaolinite system. According to the kinetic and PSI parameters for different sources adsorbed on Vertisols or the intensity and capacity factors of P-bioavailability in soils, the applied fertilizers can take the following descending order: diammonium phosphate>potassium polyphosphate>potassium dihydrogen phosphate.

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تأثير خواص الأراضى الطينية الثقيلة على ادمصاص الفوسفور

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قسم الأراضى واستغلال المياه-المركز القومى للبحوث-الجيزة-مصر.

يهدف هذا البحث إلى الوصول إلى أفضل معادلة توضح ادمصاص الفوسفور فى الاراضى الطينية الثقيلة مرتبطا بخواصها ونوع معدن الطين ولذلك طبقت اربع معادلات مع ثلاثة أنواع من ألاسمده الفوسفاتية وهى بوتاسيوم دى هيدروجين فوسفات ، بوتاسيوم دى امونيوم فوسفات ، بوتاسيوم بولى فوسفات وأيضا مع معادن الطين السائدة : المنتمور يللونيت ، الكاؤولينيت ، الاليت . وقد دلت النتائج على أن افضل معادلة يمكن تطبيقها على التربة ومعادن الطين كانت Elovich ومن دليل ادمصاص الفوسفور لمعادن الطين ومعادلات الادمصاص للتربه امكن ترتيب افضليه السماد ترتيبا تنازليا كالاتى : بوتاسيوم دى امونيوم فوسفات > بوتاسيوم بولى فوسفات > بوتاسيوم دى هيدروجين فوسفات .