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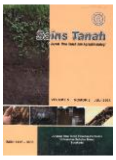

Effect of soil properties on phosphate desorption from some cultivated soils in arid region

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ABSTRACT

Kinetics of soil chemical processes is one of the most important areas in environmental chemistry for metals availability in soils and mechanisms of desorption. Phosphorus (P) is one of the most important macronutrients that control plant growth and crop production. The present study aims to evaluate the influences of soil properties of Alluvial (*Typic torrerets*) and calcareous (*Typic calcids*) on the Kinetics of P desorption using batch and anion exchange resin techniques used for P adsorption, which is highly correlated with P uptake by growing plants. Results indicated that P desorption was best described by empirical modified Freundlich (power function) and Elovich equations and, to a lesser degree, by theoretical diffusion and first-order equations. The rate of P desorption from the alluvial soils was positively and highly correlated and largely controlled by clay content ($r=0.96^{**}$) and surface area ($r=0.87^{**}$), as indicated by the simple correlation coefficient and R^2 in the multiple stepwise regression analysis. These soil properties largely controlled the variations in the kinetic parameters that describe the rate of P desorption and P intensity in the four tested kinetic models. On the other hand, calcium phosphate and active $CaCO_3$ contents in the calcareous soils were negatively correlated. They largely controlled the variations in the rate and intensity parameters of the kinetic models. These results suggest that surface precipitation on the $CaCO_3$ surface controls P desorption in calcareous soils, while reversibly, phosphate adsorption on the clay surface controls P desorption in the alluvial soils, which decreases in both cases, crop production.

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1. INTRODUCTION

In Egypt, Elkhouly et al. (2021) showed that the calcareous soils occupy about 0.65 million acres as they formed along the Mediterranean littoral of the northern part of the Western Desert. Other areas, such as the Eastern Desert and Sinai, are covered with calcareous soils. Wahba et al. (2019) studied the calcareous soils and recorded that the high pH value results in the unavailability of phosphate (formation of unavailable calcium phosphate as apatite) and usually results in reduced availability of micronutrients, iron and zinc, for example.

Phosphorus (P) is an essential plant nutrient driving growth and causes nutritional problems if released to soil-plant ecosystems in low concentration (Mayakaduwa et al., 2023; Rassaei et al., 2020). In this context, Zhang et al. (2021) considered that up to two-thirds of agricultural soils worldwide are affected by P deficiency. Statistics show that the global consumption of inorganic phosphate fertilizer (P_2O_5) increased by 34.5 million tons from 1961 to 2019 (Xiaohui Chen et al., 2022). Excessive use of P fertilizers in intensive agricultural systems has led to P accumulating in soil and releasing P to surface water, causing eutrophication of aquatic environments (van der Salm et al., 2017). Adsorption to and desorption from soil play a crucial role in the environmental behavior of inorganic P (Ghodszad et al., 2022).

The adsorption to and desorption from solid phases are key aspects of the behavior of P in soil. In the current study, desorption is more important than adsorption because of the importance of immobilized P in soil becoming available for reuse and the environmental problems P released from soil can cause. Adsorption can limit the phyto availability of P, and desorption can allow P to be lost in soil (Wang & Liang, 2014). Also, the effectiveness with which P is adsorbed will depend on the desorption process of P and be directly related to the supply of P from the solid to the liquid phase and the soil's buffering capacity, which will also affect the supply of P from the soil. The SOM is an important factor, through various mechanisms, affecting the adsorption and desorption of P in soil. In soil, P can be bound to soil organic matter (SOM), and the degree to which P is attracted to SOM will be influenced by the forms of P present and various biogeochemical and environmental factors such as the soil moisture, SOM, and clay contents (Zhang et al., 2014). Also, in another study, Debicka et al. (2016) found that removing SOM decreased the adsorption capacity for P in most of the top soils that were tested and increased the desorption process of P, indicating that removing SOM decreased the amount of bound P present.

Under aridic conditions, Wahba (2013) confirmed on the phosphate fertilizers are low attributed to reaction of phosphate with soil components such as pH, clay minerals and iron and aluminum oxides, the reactive surface and specifically $CaCO_3$. Also, several studies, such as Yang et al. (2023) proved that the phosphorus adsorption and desorption capacity exhibited positive correlations with free aluminum oxides, non-crystalline aluminum oxides, pH, specific surface area and the mass proportion of micro aggregate and silt + clay. The adsorption of P involves a sequence of adsorption processes, such as clay minerals and Fe/Al oxides, but only some of the adsorbed P will be available to plants. Therefore the Fe/Al oxides are important to the adsorption of phosphorus, additionally to the effects another factors such as the soil type, clay content, equilibrium pH, and the Al and Fe chemical forms present, each of which could affect the P adsorption capacity of soil (Gérard, 2016).

The type of soil can drastically affect the reaction rate. For example, in alluvial soils, sorption reaction is often more rapid on clay minerals such as kaolinite and semictite than on vermiculite (Kumari & Mohan, 2021). Metal sorption reactions on oxides and humic substances depend on the type of surface and the electronegativity of the metal(s), but the reaction rate appears to be rapid. Xiong et al. (2022) studied phosphate retention and desorption in clay minerals, and they found that the capacity and strength of P retention varied among the type of clay minerals in the studied soils. Regarding the type of soil, (Sun et al., 2020) studied the soil properties that are generally considered to have a greater impact on phosphorus adsorption and desorption in erosive weathered granite soil (TL-Tillage layer, LL-Laterite layer, and SL-Sand layer). Derived from the Langmuir adsorption isotherm, the maximum absorption capacity of phosphorus in TL soil was greater than that in LL and SL soil. With a pH of 4.3–5.0, the three soils have the most phosphorus adsorption. The desorption ratio in the SL soil is larger than in the LL and TL soil. On the other hand Zhou et al. (2022) studied the effect of different types of phosphate fertilizers on soil P adsorption was mainly through regulation of soil organic matter(SOM) and Olsen P, and the effect on soil P desorption was mainly through regulation of SOM and $CaCO_3$. Al_2O_3 had the greatest effect on P adsorption with a relative contribution rate of 31.52%, and SOM had the greatest effect on P desorption with a relative contribution rate of 53.04%.

Mayakaduwa et al. (2023) reported that the sorption/desorption of phosphorus by colloids in solution was significant and more of the phosphorus was adsorbed by the colloids and this was attributed to the surface charge characteristics and their relationships to minerals for each soil. In this regard, other researchers have found that the main components involved in P adsorption and surface charge are the types and amounts of the dominant clay minerals, and the various oxides (Abhiram & Eeswaran, 2022).

The overall picture, adsorption could restrict the availability of P, whereas desorption might increase the effectiveness of P. More importantly, soil physical properties such as aggregate distribution are linked to specific surface area, which is an essential indicator for determining the P adsorption and desorption capacity (Sun et al., 2022). Therefore, conservation tillage is beneficial to optimizing soil aggregate structure, thus changing the P adsorption and desorption characteristics (Sokolowski et al., 2020; Zhu et al., 2022).

In this context, most studies on adsorption and desorption capacity focus on the soil particle scale as mention by Pradhan et al. (2021). On the other hand, soil structure is closely related to chemical properties, including organic matter, iron and aluminum oxides, and total P content (Zhang et al., 2018). Accumulated studies have shown that the P adsorption and desorption capacity strongly depend on these chemical properties (Amarh et al., 2021; Xuemei Chen et al., 2022; Pradhan et al., 2021).

2.MATERIAL AND METHODS

2.1. Description of study sites and Soil sampling

Ten surface soil samples (0-30 cm) were collected from Menoufia Governorate, Egypt Latitude: 30°35'50.09"N and Longitude: 30°59'15.48"E to represent Nile Delta cultivated alluvial soils calcified as *Typic torrerts* according to soil taxonomy (Soil Survey Staff, 2022). The selected soils vary in their clay content, P content and other related properties. Also, eight calcareous surface soil samples (0-30 cm) were collected from Marute, Egyptian North coastal Latitude: 31° 0′ 30.3″ N and Longitude: 29° 45′ 34.2″ E to represent west Delta calcareous soils, classified as*Typic calcids* (Figure 1). This type of soil mainly varies in $CaCO_3$ content, textural class land use and P content. All soil samples were analyzed for their soil properties such as pH, clay content, organic matter, total and active $CaCO_3$ content, surface area, inorganic phosphate fractions (Ca-P, Al-P, &Fe-P) and amorphous Al_2O_3, Fe_2O_3 and SiO_2 corresponding to Jackson (2005) and presented in (Table 1). The soil samples were air dried, crushed sieved through a 0.5 mm sieve, mixed thoroughly, and kept in plastic jars.

2.2. Method used for P-desorption

Three grams of air-dried soil was placed in 250 ml of Erlenmeyer flask & 50 ml distilled water was added. To each flask 3 g of Dowex 1 x 8-anion exchange resin in Cl form was added. The flasks were vigorously shaken for time intervals; (a) 1, 5, 10, & 30 min, (b) 1, 2, 4, & 6 hrs., and (c) 1, 2, 4, 7, 10, & 14 days. The resin was separated from the suspension using a 0.5-mm sieve. The soil particles were removed from the resin by a stream of distilled water and the phosphate was extracted from the resin by $1N Na_2SO_4$and analyzed in the extract using batch technique and Anion Exchange Resin method described by Amer et al. (1955).

Figure 1. Locations of Alluvial and calcareous soil sampling

2.3. Kinetic models used to describe P desorption from selected soils

The P desorption data were fitted, using regression analysis to the four kinetic models, namely, modified Freundlich equation (power function) (Eq. 1), Elovich (Eq. 2), parabolic diffusion (Eq. 3), and the first-order equations (Eq. 4). In four equations, the amount of phosphate desorbed (q) at time t is related to the kinetic parameters.

Modified Freundlich ($q= K_d\, t\, b^{\backslash}$) [1]

Elovich equations ($q = 1/ß \ln αß +1/β \ln t$) [2]

Parabolic diffusion ($q = b + R\, t^{0.5}$) [3]

First-order kinetic equations ($\log q_0 – q) = \log q_0 – k_1 t$ [4]

Where q= the amount of phosphate desorption in time t; k_d= desorption rate coefficient in mg kg^{-1} soil min^{-1}; $b^{\backslash}$= intensity constant in mg P kg^{-1} soil; α = a constant related to the initial rate of P desorption in mg P kg^{-1} min^{-1}; β = 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}; q_0 = the maximum amount of P desorption in mg P kg^{-1} soil; k_1 = the rate constant of the reaction in sec^{-1}.

The constants describing the rate of P desorption and those representing P capacity were calculated and correlated with soil properties using Microsoft Excel (Jelen, 2010). The stepwise multiple regression analysis was also carried out between each of these kinetic parameters and those soil properties that gave significant r values with it in an attempt (Turaev, 2019) to identify soil properties that affect the rate of P desorption most.

3. RESULTS

Table 2 shows that the P desorption data from alluvial soils (*Typic torrerets*) and calcareous soils (*Typic calcids*) can be described by the empirical modified Freundlich and Elovich kinetic equations judging by the higher values of R^2 and the lower values of the standard error (SE). The parabolic diffusion and the first-order equations gave lower and sometimes insignificant R^2.

Table 1. Some properties of the investigated soils

Soil Property	Alluvial soils		Calcareous soils	
	Range	Mean	Range	Mean
PH (1-2.5)	7.1-7.94	7.52	7.24-7.95	7.60
$CaCO_3$ (%)	2.25-3.91	3.08	10.40-77.25	44.33
Active $CaCO_3$ (%)	1.75-3.57	2.66	4.58-17.90	11.24
Organic matter (%)	0.29-0.73	0.51	0.03-0.75	0.39
Surface area ($m^2\,g^{-1}$)	120-210	165	62-170	116
Available P (ppm)	30-55	44	14-35.5	24.75
Clay content (%)	26.65-42.00	34.33	11.80-35.5	23.65
P- Fractions (mg kg^{-1})				
Al-P	13.00-26.00	19.5	11.00-34.00	22.5
Fe-P	27.50-46.00	36.75	12.00-35.00	23.5
Ca-P	119.00-171.00	145	21.00-100.00	60.5
Amorphous materials (mg kg^{-1})				
Fe_2O_3	0.11-0.46	0.29	0.20-0.48	0.34
Al_2O_3	13.10-32.80	22.95	5.60-14.20	9.9
SiO_4	1.90-6.13	4.02	0.10-0.37	0.24

Table 2. Ranges of coefficients of determination R^2& standard error (SE) of the fit P-desorption data from soils to the different kinetic models

Kinetic model	Alluvial soils		Calcareous soil	
	R^2	SE	R^2	SE
M. Freundlich	0.83**-0.91**	0.06-0.13	0.89^{**}-0.96^{**}	0.03-0.08
Elovich	0.95**-0.98**	1.35-5.07	0.97^{**}-0.99^{**}	0.40-1.09
Diffusion	0.51^{ns}-0.70**	3.90-9.92	0.67^{*}-0.81^{**}	1.26-4.61
First-order	0.55^{ns} -0.79**	0.39-0.81	0.49^{ns}-0.83^{**}	0.25-0.50

Table 3. Kinetic parameters for several equations described phosphate desorption from alluvial soil samples

Soil No.	Modified equation Freundlich		Parabolic diffusion equation		Elovich equation		1^{st}. order equation	
	k_d	$b^{\backslash}$	b	R	α	β	V	$K*10^5$
1	0.16	7.59	14.80	0.15	27.90	0.38	2.68	23
2	0.15	12.58	24.71	0.16	75.70	0.26	2.69	45
3	0.13	15.85	26.75	0.21	146.90	0.26	3.05	39
4	0.16	6.46	13.28	0.12	26.50	0.44	2.43	28
5	0.12	15.13	25.14	0.19	201.40	0.29	2.92	35
6	0.20	5.37	13.43	0.15	11.80	0.36	2.66	40
7	0.14	7.41	21.91	0.11	59.40	0.52	2.38	31
8	0.13	10.47	18.25	0.14	105.80	0.39	2.49	37
9	0.15	8.40	15.78	0.14	6.97	0.39	2.85	38
10	0.14	15.85	27.13	0.23	115.95	0.24	3.10	40

Table 4. Correlation coefficient (r) between the rate constants of selected equations described the kinetics of P-desorption from alluvial clay soils.

Parameter	Modified Freundlich equation		Parabolic diffusion equation		Elovich equation		1st. order equation	
	$b^{\backslash}$	k_d	b	R	α	β	v	k
$b^{\backslash}$		-0.34^{ns}	-0.21^{ns}	0.30^{ns}	-0.40*	0.57**	0.40*	0.46*
K_d			0.91^{***}	0.69^{***}	0.87^{***}	-0.48^{**}	0.30^{ns}	0.44^{*}
b				0.62^{***}	0.80^{***}	-0.34^{ns}	0.44^{*}	0.47^{**}
R					0.54^{**}	-0.01^{ns}	0.61^{***}	0.64^{***}
α						-0.32^{ns}	0.29^{ns}	0.26^{ns}
β							0.55^{**}	0.10^{ns}
V								0.52^{**}
K								

3.1. Alluvial soils

The kinetic parameters that describe the rate of P desorption in soil according to the modified Freundlich equation (k_d), Elovich (β), and the parabolic diffusion (R) equations were calculated (Table 3) and found at 0.001 level highly correlated with clay content, surface area, available P, Ca-P, Fe_2O_3, active $CaCO_3$and organic matter content in the alluvial soils of Nile Delta, but negatively correlated with Fe-P content (Table 4). The β value of Elovich equation reported to be inversely related to the rate of P desorption in soil was found to be inversely related to the above-mentioned soil properties. The correlation coefficient was highest with clay content, surface area, available P, Fe_2O_3, and organic matter and followed the order of $K_d>\alpha>R>\beta$. However, the rate constants of the first–order equation had a relatively poor correlation with these soil properties. It is interesting to note that the constants representing the intensity of P in the kinetic equation, such as $b^{\backslash}$ in the modified Freundlich, b in the parabolic diffusion, and q_0 in the first-order equations, also had a highly significant correlation with the same soil properties that correlated highly with rate parameters of P-desorption (Table 4). The correlation coefficient was higher with the b value of the diffusion equation followed by the $b^{\backslash}$ value of the modified Freundlich equation and least with q_0 of the first-order kinetic equation. The rate of P- desorption coefficient of the modified Freundlich equation (k_d) held the highest r values among all the above-mentioned parameters. It should be recalled that the modified Freundlich and Elovich equations offered the best fit to the P-description data in the alluvial soil of Nile Delta (Table 3).

The correlation analysis (Table 4) shows that most of the kinetic parameters describing the rate of P desorption in the tested models are significantly correlated. For example, the apparent rate of P desorption in the modified Freundlich equation, Kd, was highly correlated (at 0.001 level) with the diffusion rate coefficient (R) in the diffusion equation, and the initial rate of P desorption (α) in the Elovich equation. It also inversely correlated (at 0.01 level) with the β value of Elovich equation and with the first-order rate constant R (at 0.05 level). The R-value was also significantly correlated with α (0.001 level), k_d (0.001 level), and k_1 (0.001 level), whereas the k_1 was significantly correlated with R (0.001 level) and k_d (0.05 level). It is also noted that these kinetic parameters were correlated with most of the P intensity parameters in the tested equations, especially the b value in the diffusion equation, at various significance levels.

The stepwise multiple regression analysis was conducted to identify soil properties that affect the rate of P desorption most. Focus, of course, will be on those kinetic parameters that affect the rate of P-desorption in modified Freundlich and Elovich equations, which offered the best fit for the P-description data. The R^2 values between the kinetic parameter of P desorption as a dependent variable and the soil properties as independent variables are shown in Table 5.

Table 5. Stepwise regression analysis relating kinetic parameters with alluvial soil properties

Equation	Kinetic parameter	Step No.	Step-wise regression equation	R^2
Modified Freundlich Equation	k_d	S1	k_d = 0.71 clay – 14.63	0.96**
		S2	k_d = 0.39 clay + 0.1Ca- p-17.81	0.97**
	$b^{\backslash}$	S1	$b^{\backslash}$ =0.003clay + 0.26	0.66**
		S2	$b^{\backslash}$ =0.01clay + 0.05Fe_2O_3 + 0.38	0.80**
		S3	$b^{\backslash}$=0.01clay+0.001CaP+0.077 Fe_2O_3 +0.46	0.84**
		S4	$b^{\backslash}$ = 0.001 S. area - 0.014 Clay - 0.001Ca-P +0.007 Fe_2O_3 + 0.50	0.87**
Parabolic diffusion Equation	R	S1	R = 0.16 OM + 0.07	0.56**
		S2	R = 0.18 OM + 0.23Fe_2O_3 - 0.02	0.76**
	b	S1	b =0.09 S. area + 4.72	0.83**
		S2	b =0.40 S. area - 1.13 Avail - P + 1.71	0.86**
Elovich equation	β	S1	β = -0.009 Fe2O3 + 0.55	0.40*
	α	S1	α = 9.92 Clay – 270.05	0.73**
		S2	α = -3.1 S. area + 26.9Clay - 374	0.76**
1st order	k	S1	k = 12.57 A.$CaCO_3$ + 4.36	0.57**
	V	S1	v = 0.013 Ca-P + 0.79	0.57**
		S2	v = 0.028 Ca- P - 0.07 Fe2O3 +0.08	0.68**

Table 6. Kinetic parameters of different equations described phosphate desorption from Calcareous soil samples

Soil	Modified Freundlich equation		Parabolic diffusion equation		Elovich equation		1st. order equation	
No.	k_d	$b^{\backslash}$	b	R	α	β	V	$K*10^5$
1	0.11	11.22	10.69	0.12	19.65	0.50	2.60	27
2	0.14	3.01	17.16	0.12	5.82	0.47	2.42	42
3	0.14	3.00	5.02	0.05	15.89	1.19	1.71	26
4	0.13	3.50	5.85	0.05	36.48	1.21	1.46	24
5	0.11	11.48	17.10	0.13	177.93	0.44	2.61	30
6	0.14	5.05	8.55	0.09	19.49	0.66	2.28	31
7	0.16	7.08	13.57	0.13	36.04	0.49	2.57	37
8	0.14	8.51	14.39	0.15	34.62	0.41	2.74	32

These results indicate that K_d; the apparent rate of P-desorption coefficient in modified Freundlich equation was most influenced by clay content ($R^2 = 0.96^{***}$). Including Ca-P raised R^2 only to 0.97^{***}.Clay content was also the most effective soil property affecting P intensity as desorbed by the $b^{\backslash}$ parameter (R^2= 0.66^{***}) followed by the Fe_2O_3 content, Ca-P and surface area.

The α parameter in Elovich equation related to the initial rate of P desorption (Claveau-Mallet et al., 2014) was mainly controlled also by clay content ($R^2 = 0.73^{***}$). This means that 73% of the variation in α is attributed to clay content. Including the surface area of the soil raised R^2 to noly 0.76^{***}. On the other hand, the β value in Elovich equation is negatively related to the supplying power of soil P (Sundha et al., 2022)and the rate of P desorption was correlated by Fe_2O_3% (R^2= 0.40*). The diffusion rate coefficient R, was controlled most by the organic matter and Fe_2O_3 contents ($R=76^{***}$) whereas the P intensity parameter, b, was highly controlled by surface area ($R=0.83^{***}$) which is apparently related to the clay content. The first-order rate constant, k_1 was only primarily controlled by active $CaCO_3$ % whereas q, the P intensity represented by q_0 was primarily controlled by Ca –P. It should be mentioned that tested alluvial soil varied slightly by OM, Fe_2O_3 and active $CaCO_3$.

3.2. Calcareous soil

Unlike the alluvial soils, only available P was positively and significantly correlated with most kinetic parameters describing the rate of P desorption in calcareous soils (Table 6). The correlation coefficient was significant at 0.001 level for k_d, 1/β, and R and at 0.05 level with α.

Stepwise multiple regression analysis with the kinetic parameters as dependent variables and soil properties as independent variables (Table 7 and Figure 3) shows that Ca-P and active $CaCO_3$ contents are the major factors controlling P-desorption in calcareous soils. Both factors negatively affected the rate of P-desorption as measured by k_d, R, 1/βand k1 in the four tested models. For example, Ca-P controlled 94% of the variation in k_d whereas 84% of the variations in R andβ were attributed to active $CaCO_3$ content. It is interesting to note that Ca-P or active $CaCO_3$ contents also controlled the P intensity in calcareous soils as measured by $b^{\backslash}$ in modified Freundlich equation, b in the diffusion equation and q_0 in the first-order equation.

Table 7. Stepwise regression analysis relating kinetic parameters in the tested equation with calcareous soil properties

Equation	Kinetic parameter	Step No.	Step-wise regression equation	R^2
Modified Freundlich equation	k_d	s_1	k_d = -0.14 Ca-P + 14.70	0.94**
		s_2	k_d =0.156 Avail- p - 0.07 Ca-P +7.19	0.99**
	$b^{\backslash}$	s_1	$b^{\backslash}$ = -0.12 Ca-P + 14.76	0.96^{**}
		s_2	$b^{\backslash}$ = 0.16 Avail-P - 0.07Ca-P + 7.46	0.99^{**}
Parabolic diffusion equation	R	s_1	R = -0.007 A.$CaCO_3$ + 0.17	0.84**
		s_2	R = -0.005 A.$CaCO_3$ + 0.002avail P+0.12	0.93**
	b	s_1	b = -0.88 A.$CaCO_3$ + 20.28	0.91**
Elovich equation	β	s_1	B = 0.061A.$CaCO_3$ + 0.065	0.84**
		s_2	B = 0.052A.$CaCO_3$ - 0.008Avail- P +0.34	0.86**
	α	s_1	α = -4.42Fe-P + 162.9	0.48^{ns}
First order equation	k	s_1	k = -0.77A.$CaCO_3$ + 3.1	0.45^{ns}
		s_1	v = -0.08A.$CaCO_3$ + 3.1	0.80**
	V	s_2	v= -0.06A.$CaCO_3$ + 0.02Avail- P + 2.42	0.92**

Remarks: ns: non-significant**: significant at 0.01 level

Calcium phosphate was responsible for 96% of the variations in $b^{\backslash}$ whereas active $CaCO_3$ controlled 91% of the variation in b and 80% of the variation in q_0.

Calcium phosphate was found to be the dominant inorganic phosphate fraction in the calcareous soils of Egypt (Hejazi Mehrizi et al., 2015). Mahdi and Mouhamad (2018) showed that Ca-P represented 78% of the total inorganic phosphate in these soils. Those results suggested that phosphate precipitation on the surface of $CaCO_3$ is the dominant reaction taking place under the condition of calcareous soils and that relatively revisable adsorption of phosphate on clay surface is the dominant reaction taking place under the condition of the alluvial soils of Nile Delta.

4. DISCUSSION

The kinetics of phosphate release from two different soils were studied using the anion exchange resin technique by measuring the amount of P extracted by the Cl-resine at time intervals ranging between 1min and 14 days to understand the most factors controlling P fixation and subsequently P bioavailability. The two soils were an alluvial clay soil from Menofya (*Typic torrert*) and calcareous loam soil from Mariot (*Typic calcid*). Numerous models have been developed to quantitatively describe nutrient desorption isotherms, namely Modified Freundlich, Elovich, parabolic diffusion, and 1st-order equations.

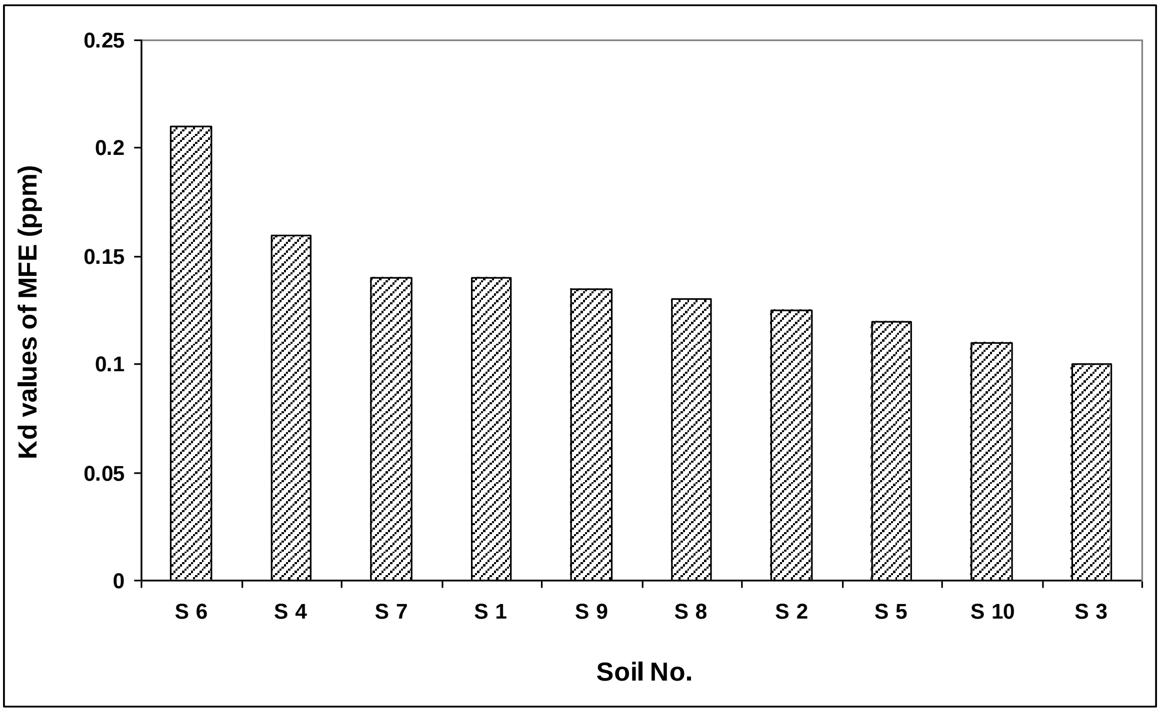

Figure 2. Relationship between increasing clay contents in used soils (S) &MFE rate constant (kd) of P desorption

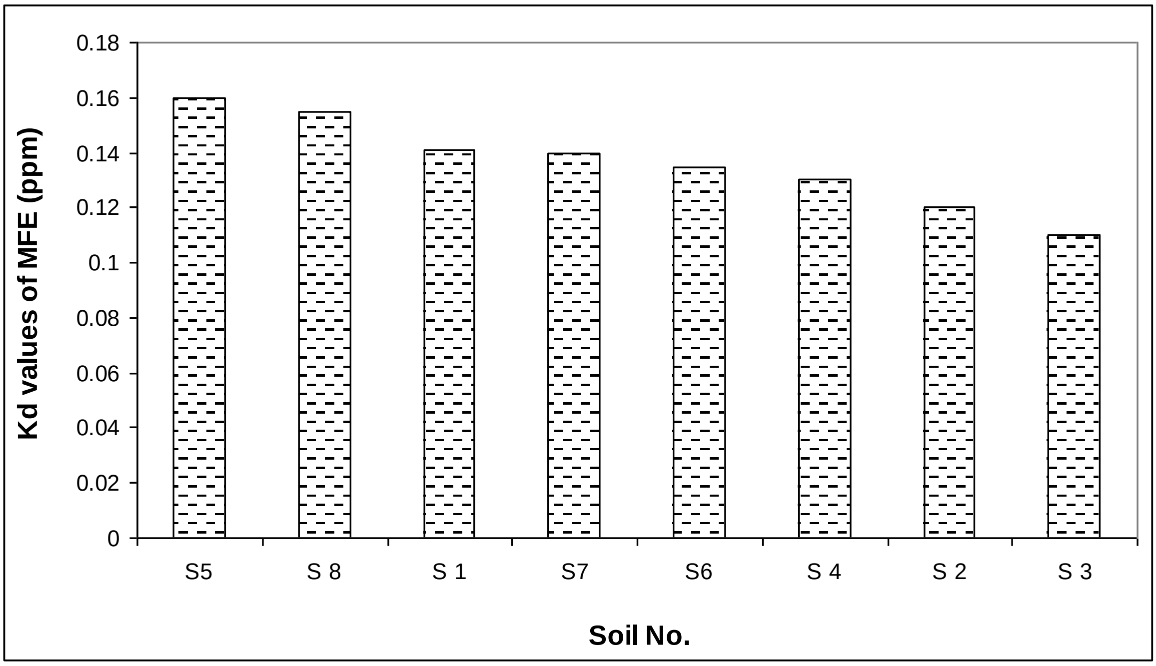

Figure 3. Relationship between increasing of A. $CaCO_3$ in used soils (S) & rate of P desorption Kd values of MFE

The behavior of P release in all soils varied widely with the soil type studied. Results showed that phosphate desorption from alluvial soils was significantly ($P<0.05$) influenced by clay content (Figure 1), surface area, and Fe_2O_3 (amorphous materials), increasing these soil components significantly ($P<0.05$) decreased the rate of P desorption (El–Kherbawy et al., 2014; Sparks, 2013), they interlayer hydroxy hypothesized that -Al and hydroxy-Fe polymers in clay minerals may be important for P mobility and availability in alluvial clay soils by trapping P in an occluded form. In addition, the presence of Ca in the soil ecosystem significantly minimizes the rate of P desorption through the formation of Ca-P precipitate (Barrow & Debnath, 2014; Ye et al., 2022). This result was confirmed in our work in the step-wise regression, where the capacity factor v of the 1st-order model is significantly controlled by Ca-P. Organic matter contents in selected alluvial soils also influenced the rate of P desorption through the (R) constant of diffusion kinetic model. Yang et al. (2019) showed that the ratio of soil P desorption was the greatest when the soil organic matter SOM content decreased in black soil. Moreover, in alluvial soil, clay content becomes the most important factor in controlling P desorption. The step-wise regression showed that the rate of P desorption K_d of MFE was significantly controlled by clay content in S_1 followed by Ca-P in S_2. Chintala et al. (2014) and Eduah et al. (2019) mentioned that Phosphorus desorption by various alluvial soils studied seems to be controlled by anion exchange between anions of P react with the oxygenated functional groups on the surface of clay beside the residence type.

The conformity of kinetic data to Elovich, power function and parabolic diffusion equations may indicate that the diffusion process might be the rate-limiting step in P release from the soils. Also proposed that Elovich equation applies to diffusion controlled sorption–desorption reactions. The close relationship (r =0.99**) between the Elovich equation 1/β and the overall diffusion constant R may demonstrate this idea.

Stepwise multiple regression analysis indicates that k_d constant is most influenced by clay content (R^2 = 0.96**). The b$^\backslash$ was influenced by clay content, amorphous iron oxide, and calcium phosphate. The R kinetic parameter of the parabolic diffusion equation is mainly affected by OM content in the first step and highly affected by both OM and amorphous iron oxide in the second step (R^2 = 0.76). Also, the b constant was highly and significantly affected by surface area (R^2 = 0.83). The kinetic parameters, the constants representing the rate of P-release in the tested equations (k_d, 1/ β, α, R and to a less extent k in modified Freundlich, Elovich, parabolic diffusion and first-order equations, respectively) and also constants describing P-intensity such as b in parabolic diffusion and V in the first-order equation were all positively and significantly correlation (at 0.001 level) with clay content, surface area, available P in alluvial soil. Clay content, which controls surface area in soil, is one of the most important factors influencing the rate of phosphate exchange as well as the equilibrium concentration of P in soil. The same results were observed, Wahba et al. (2019).

Opposite to the alluvial soils, most of the kinetic parameters in calcareous soils were negatively correlated with clay content, surface area, active $CaCO_3$, Al-P, Fe-P and Ca-P with variable degrees of significance, suggesting that under the conditions of calcareous soils, phosphate precipitation on the surface of soil components rather than phosphate adsorption is the dominant reaction taking place (Figure 2). The same results were documented by Ozyhar et al. (2022).

The β constant of Elovich equation which is correlated with P-supplying power was only influenced by amorphous iron oxide with a low significant coefficient of determination (R^2 = 0.57) the constant α of Elovich equation is highly influenced by clay content. The first-order equation k_{-1} was only influenced by the active $CaCO_3$ content, but the intensity factor V was primarily dependent on calcium phosphate content Sherine et al. (2014).

Unlike the alluvial soils only available P had a positive and significant correlation with most kinetic parameters of the four tested equations. The correlation coefficient was significant at 0.001 level for k_d, $1/\beta$, V and R and at 0.05 level for α and β and insignificant with $b^\backslash$ and k. Stepwise multiple regression analysis shows that the apparent desorption rate coefficient k_d in the modified Freundlich equation was influenced mostly by phosphate content in the calcium form. The β constant of the Elovich equation was mainly influenced by active $CaCO_3$ since eighty-four percent of the variation in β was controlled by active $CaCO_3$. Active $CaCO_3$ and the available P were the soil properties that influenced the kinetic parameter R of phosphate desorption most in the parabolic diffusion equation. The V value which is the intensity parameter was again controlled by active calcium carbonate and the available P. According to above mentioned results application of P fertilizer in alluvial soils must be controlled by understanding the soil properties controlled the P bioavailability.

5. CONCLUSION

In this work, results imply that desorption of phosphate from alluvial soils could mainly depend on clay content, surface area, and Fe oxide amorphous material, while P desorption from calcareous soil depends on active $CaCO_3$and available P. Application of phosphate fertilizers in alluvial and calcareous soils must be based on understanding the most soils properties controlled P bioavailability. In addition, kinetic models used well described the rate of P desorption from used soils with priority to Modified Freundlich Equation (MFE) in both types of soils.

Declaration of Competing Interest

The authors declare that no competing financial or personal interests that may appear and influence the work reported in this paper.

References

Abhiram, G., & Eeswaran, R. (2022). Chapter 4 - Legumes for efficient utilization of summer fallow. In R. S. Meena & S. Kumar (Eds.), *Advances in Legumes for Sustainable Intensification* (pp. 51-70). Academic Press. https://doi.org/10.1016/B978-0-323-85797-0.00009-4

Amarh, F., Voegborlo, R. B., Essuman, E. K., Agorku, E. S., Tettey, C. O., & Kortei, N. K. (2021). Effects of soil depth and characteristics on phosphorus adsorption isotherms of different land utilization types: Phosphorus adsorption isotherms of soil. *Soil and Tillage Research*, *213*, 105139. https://doi.org/10.1016/j.still.2021.105139

Amer, F., Bouldin, D. R., Black, C. A., & Duke, F. R. (1955). Characterization of soil phosphorus by anion exchange resin adsorption and P32-equilibration. *Plant and Soil*, *6*(4), 391-408. https://doi.org/10.1007/BF01343648

Barrow, N. J., & Debnath, A. (2014). Effect of phosphate status on the sorption and desorption properties of some soils of northern India. *Plant and Soil*, *378*(1), 383-395. https://doi.org/10.1007/s11104-014-2042-8

Chen, X., Yan, X., Wang, M., Cai, Y., Weng, X., Su, D., . . . Zhang, F. (2022). Long-term excessive phosphorus fertilization alters soil phosphorus fractions in the acidic soil of pomelo orchards. *Soil and Tillage Research*, *215*, 105214. https://doi.org/10.1016/j.still.2021.105214

Chen, X., Zhang, W., Gruau, G., Couic, E., Cotinet, P., & Li, Q. (2022). Conservation practices modify soil phosphorus sorption properties and the composition of dissolved phosphorus losses during runoff. *Soil and Tillage Research*, *220*, 105353. https://doi.org/10.1016/j.still.2022.105353

Chintala, R., Schumacher, T. E., McDonald, L. M., Clay, D. E., Malo, D. D., Papiernik, S. K., . . . Julson, J. L. (2014). Phosphorus Sorption and Availability from Biochars and Soil/Biochar Mixtures. *CLEAN – Soil, Air, Water*, *42*(5), 626-634. https://doi.org/10.1002/clen.201300089

Claveau-Mallet, D., Courcelles, B., & Comeau, Y. (2014). Phosphorus Removal by Steel Slag Filters: Modeling Dissolution and Precipitation Kinetics to Predict Longevity. *Environmental Science & Technology*, *48*(13), 7486-7493. https://doi.org/10.1021/es500689t

Debicka, M., Kocowicz, A., Weber, J., & Jamroz, E. (2016). Organic matter effects on phosphorus sorption in sandy soils. *Archives of Agronomy and Soil Science*, *62*(6), 840-855. https://doi.org/10.1080/03650340.2015.1083981

Eduah, J. O., Nartey, E. K., Abekoe, M. K., Breuning-Madsen, H., & Andersen, M. N. (2019). Phosphorus retention and availability in three contrasting soils amended with rice husk and corn cob biochar at varying pyrolysis temperatures. *Geoderma*, *341*, 10-17. https://doi.org/10.1016/j.geoderma.2019.01.016

El–Kherbawy, M. I., Abou-Zeid, S. T., El-Aila, H. I., Afify, R., & Zaghloul, A. (2014). Chemical Characterization of Phosphate Rock Applied in Arid Region. *Middle East Journal of Agriculture Research*, *3*(1), 59-70.

Elkhouly, A. A., Omran, E.-S. E., & Negm, A. (2021). Introduction to "Management and Development of Agricultural and Natural Resources in Egypt's Deserts". In A. A. Elkhouly & A. Negm (Eds.), *Management and Development of Agricultural and Natural Resources in Egypt's Desert* (pp. 3-14). Springer International Publishing. https://doi.org/10.1007/978-3-030-73161-8_1

Gérard, F. (2016). Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils — A myth revisited. *Geoderma*, *262*, 213-226. https://doi.org/10.1016/j.geoderma.2015.08.036

Ghodszad, L., Reyhanitabar, A., Oustan, S., & Alidokht, L. (2022). Phosphorus sorption and desorption characteristics of soils as affected by biochar. *Soil and Tillage Research*, *216*, 105251. https://doi.org/10.1016/j.still.2021.105251

Hejazi Mehrizi, M., Sarcheshmehpour, M., & Ebrahimi, Z. (2015). The effects of some humic substances and vermicompost on phosphorus transformation rate and forms in a calcareous soil. *Journal of soil science and plant nutrition*, *15*, 249-260. https://doi.org/10.4067/S0718-95162015005000020

Jackson, M. L. (2005). *Soil Chemical Analysis: Advanced Course. UW-Madison Libraries Parallel Press, 2005*. UW-Madison Libraries parallel press.

Jelen, M. E. B. (2010). *Microsoft® Excel 2010 In Depth*. Pearson Education Incorporated. https://books.google.co.id/books?id=xsLktwEACAAJ

Kumari, N., & Mohan, C. (2021). Basics of Clay Minerals and Their Characteristic Properties. In N. Gustavo Morari Do (Ed.), *Clay and Clay Minerals* (pp. Ch. 2). IntechOpen. https://doi.org/10.5772/intechopen.97672

Mahdi, H. H., & Mouhamad, R. S. (2018). Behavior of phosphorus in the calcareous soil. *Advances in Agricultural Technology & Plant Sciences*, *1*(4), 180018. https://academicstrive.com/AATPS/AATPS180018.pdf

Mayakaduwa, M. A. P., Rafii, Y. M., Ismail, R., Liyanage, L. R. M. C., Rupasinghe, M. G. N., & Hanafi, M. M. (2023). Identification of Phosphate Sorption-Desorption and Accumulation Characteristics to Reduce Environmental Consequences. *Communications in Soil Science and Plant Analysis*, *54*(7), 926-944. https://doi.org/10.1080/00103624.2022.2137182

Ozyhar, T., Marchi, M., Facciotto, G., Bergante, S., & Luster, J. (2022). Combined application of calcium carbonate and NPKS fertilizer improves early-stage growth of poplar in acid soils. *Forest Ecology and Management*, *514*, 120211. https://doi.org/10.1016/j.foreco.2022.120211

Pradhan, S. N., Ghosh, A. K., Seema, Ram, S., Pal, Y., & Pradhan, C. (2021). Changes in degree of phosphorus saturation and risk of P loss upon twelve years of manuring and reduced tillage. *Geoderma*, *404*, 115277. https://doi.org/10.1016/j.geoderma.2021.115277

Rassaei, F., Hoodaji, M., & Abtahi, S. A. (2020). Fractionation and mobility of cadmium and zinc in calcareous soils of Fars Province, Iran. *Arabian Journal of Geosciences*, *13*(20), 1097. https://doi.org/10.1007/s12517-020-06123-x

Sherine, S. M., AbdEl-Kreim, A. M. M., Evon, K. R., & Zaghloul, A. M. (2014). Effect of Residence Time & Soil Temperature on Phosphate Release from Treated Soils with Phosphocompos. *Middle East Journal of Applied Sciences*, *4*(3), 520-527.

Soil Survey Staff. (2022). *Keys to Soil Taxonomy* (13th ed.). USDA-Natural Resources Conservation Service. https://www.nrcs.usda.gov/sites/default/files/2022-09/Keys-to-Soil-Taxonomy.pdf

Sokolowski, A. C., Prack McCormick, B., De Grazia, J., Wolski, J. E., Rodríguez, H. A., Rodríguez-Frers, E. P., . . . Barrios, M. B. (2020). Tillage and no-tillage effects on physical and chemical properties of an Argiaquoll soil under long-term crop rotation in Buenos Aires, Argentina. *International Soil and Water Conservation Research*, *8*(2), 185-194. https://doi.org/10.1016/j.iswcr.2020.02.002

Sparks, D. L. (2013). *Kinetics of soil chemical processes*. Academic press.

Sun, T., Deng, L., Fei, K., Zhang, L., & Fan, X. (2020). Characteristics of phosphorus adsorption and desorption in erosive weathered granite area and effects of soil properties. *Environmental Science and Pollution Research*, *27*(23), 28780-28793. https://doi.org/10.1007/s11356-020-08867-1

Sun, T., Fei, K., Deng, L., Zhang, L., Fan, X., & Wu, Y. (2022). Adsorption-desorption kinetics and phosphorus loss standard curve in erosive weathered granite soil: Stirred flow chamber experiments. *Journal of Cleaner Production*, *347*, 131202. https://doi.org/10.1016/j.jclepro.2022.131202

Sundha, P., Rai, A. K., Basak, N., Yadav, R. K., & Sharma, P. C. (2022). P solubility and release kinetics in the leachate of saline–sodic soil: Effect of reclamation strategies and water quality. *Soil and Tillage Research*, *222*, 105440. https://doi.org/10.1016/j.still.2022.105440

Turaev, S. J. (2019). Methods of the using of software program Microsoft Excel in practical and laboratory occupation on physics. *Scientific & Technical Journal of Namangan Institute of Engineering & Technology*, *1*(10), 292-297. https://core.ac.uk/download/pdf/287379577.pdf

van der Salm, C., van Middelkoop, J. C., & Ehlert, P. A. I. (2017). Changes in soil phosphorus pools of grasslands following 17 yrs of balanced application of manure and fertilizer. *Soil Use and Management*, *33*(1), 2-12. https://doi.org/10.1111/sum.12333

Wahba, M., Labİb, F., & Zaghloul, A. (2019). Management of Calcareous Soils in Arid Region. *International Journal of Environmental Pollution and Environmental Modelling*, *2*(5), 248-258. https://dergipark.org.tr/en/pub/ijepem/issue/54370/789221

Wahba, M. M. (2013). Influence of soil components on phosphorus availability in some soils of Egypt [Article]. *Research Journal of Chemistry and Environment*, *17*(9), 58-65. https://www.scopus.com/inward/record.uri?eid=2-s2.0-84883500562&partnerID=40&md5=8130e39d17beb2e08df337851ba2386b

Wang, L., & Liang, T. (2014). Effects of exogenous rare earth elements on phosphorus adsorption and desorption in different types of soils. *Chemosphere*, *103*, 148-155. https://doi.org/10.1016/j.chemosphere.2013.11.050

Xiong, J., Liu, Z., Yan, Y., Xu, J., Liu, D., Tan, W., & Feng, X. (2022). Role of clay minerals in controlling phosphorus availability in a subtropical Alfisol. *Geoderma*, *409*, 115592. https://doi.org/10.1016/j.geoderma.2021.115592

Yang, J., Xin, X., Zhang, X., Zhong, X., Yang, W., Ren, G., & Zhu, A. (2023). Effects of soil physical and chemical properties on phosphorus adsorption-desorption in fluvo-aquic soil under conservation tillage. *Soil and*

Tillage Research, *234*, 105840. https://doi.org/10.1016/j.still.2023.105840

Yang, X., Chen, X., & Yang, X. (2019). Effect of organic matter on phosphorus adsorption and desorption in a black soil from Northeast China. *Soil and Tillage Research*, *187*, 85-91. https://doi.org/10.1016/j.still.2018.11.016

Ye, T., Min, X., Jiang, X., Sun, M., & Li, X. (2022). Adsorption and Desorption of Coal Gangue toward Available Phosphorus through Calcium-Modification with Different pH. *Minerals*, *12*(7), 801. https://doi.org/10.3390/min12070801

Zhang, S., Huffman, T., Zhang, X., Liu, W., & Liu, Z. (2014). Spatial distribution of soil nutrient at depth in black soil of Northeast China: a case study of soil available phosphorus and total phosphorus. *Journal of Soils and Sediments*, *14*(11), 1775-1789. https://doi.org/10.1007/s11368-014-0935-z

Zhang, X., Zhu, A., Xin, X., Yang, W., Zhang, J., & Ding, S. (2018). Tillage and residue management for long-term wheat-maize cropping in the North China Plain: I. Crop yield and integrated soil fertility index. *Field Crops Research*, *221*, 157-165. https://doi.org/10.1016/j.fcr.2018.02.025

Zhang, Y., Dalal, R. C., Bhattacharyya, R., Meyer, G., Wang, P., Menzies, N. W., & Kopittke, P. M. (2021). Effect of long-term no-tillage and nitrogen fertilization on phosphorus distribution in bulk soil and aggregates of a Vertisol. *Soil and Tillage Research*, *205*, 104760. https://doi.org/10.1016/j.still.2020.104760

Zhou, L., Su, L., Zhang, L., Zhang, L., Zheng, Y., & Tang, L. (2022). Effect of Different Types of Phosphate Fertilizer on Phosphorus Absorption and Desorption in Acidic Red Soil of Southwest China. *Sustainability*, *14*(16), 9973. https://doi.org/10.3390/su14169973

Zhu, D., Cong, R., Ren, T., Lu, Z., Lu, J., & Li, X. (2022). Straw incorporation improved the adsorption of potassium by increasing the soil humic acid in macroaggregates. *Journal of Environmental Management*, *310*, 114665. https://doi.org/10.1016/j.jenvman.2022.114665