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Effect of Humic Acid on Phosphate Adsorption in Calcareous Soils with Variable Caco$_3$ Content

Mohamed S. Kotb
Soil Science Department, Faculty of Agriculture, Cairo University, Giza 12613, Egypt

CALCAREOUS soil is susceptible to phosphorus deficit due to its high phosphate adsorption and fixing rate, which is mostly caused by a high concentration of phosphate adsorbent. Amorphous Al, Fe, and Mn oxides, together with $CaCO_3$, are the main phosphate adsorbents in calcareous soil. They essentially serve as the same binding or adsorbent for humic acid products. The availability and adsorption of P in agricultural soils following phosphate fertilizer treatments may therefore be hampered by humic acid (HA) in calcareous soil. The current study sought to investigate the effects of humic (HA) on phosphate competitive adsorption in calcareous soils with different $CaCO_3$ contents by administering HA at a rate of 2.5 g kg^{-1} soil. To reflect the calcareous soils of Egypt, five soil samples with varying calcium carbonate levels (10.6%, 22.1%, 31.7%, 42.5%, and 51.3%, respectively) were gathered. These samples are referred to as S_1, S_2, S_3, S_4, and S_5. This soil's phosphate adsorption isotherm was calculated using phosphorus concentrations of 0.5, 1.0, 2.5, 5.0, 10.0, 20.0, and 40 mg P L^{-1} at its natural pH values. The Langmuir and Freundlich adsorption isotherms models were used to numerically characterize the phosphate adsorption isotherm of the soil samples. To study the competitive sorption of phosphate and humic acid (HA) (order of addition), Three experiments have been carried out to predict the amount of adsorbed-P on soils in the presence of humic acid (HA) 2.5 g kg^{-1} soil, amounts of P added (5, 10, 25, 50, 100, 200, and 400 mg kg^{-1}), and order of P and HA additions. The order of addition were (i) P before humic acid (P/HA), (ii) P together humic acid (P+HA), and (iii) P after humic acid (HA/P). The results show that the effect of HA was limited at the low initial amounts of added P (25 and 50 mg kg^{-1} soil). In all soils a maximum reduction in the amount of adsorbed P occurred when HA was added before P (HA/P system) especially at the high rate of added P (400 mg kg^{-1} soil). The compared means by Least Significant Differences analysis Test (LSD$_{0.05}$), showed that the amount of P adsorbed on soils in the presence of HA (2.5 g kg^{-1} soil), significantly decreased the amount of adsorbed-P for all studied soil samples, especially when phosphors added after humic acid (HA/P) system.

Keywords: Phosphate adsorption isotherm, Competitive adsorption, humic acid, Calcareous soils.

1. Introduction

About 96% of Egypt's soil area is made up of desert soils, with limestone soils found all over the country. Enhancing the characteristics of these soils and cultivating them to increase agricultural output has become essential issue to meet the ongoing demand for food and close the food gap (Abou Hussien et al., 2019; Yassin et al., 2023). The high content of $CaCO_3$ in calcareous soils, which can reach over 15% (Abou Hussien et al., 2023; Nada et al., 2023) causes a number of physical and chemical issues in the soil, including excessive soil pH and an imbalance in the nutrients' distribution in the soil solution (Abou Hussien et al., 2019 and 2021). Soil fertility is affected by the high percentage of $CaCO_3$, which results in a reduce in agricultural crop production (Yassin et al., 2023). Phosphorus is a key nutrient for the net primary production on Earth and its abundance plays a critical role in shaping ecosystems (Walton et al., 2023). It has been estimated that 43 % of the Earth's land area is under phosphorus deficiency, particularly in tropical soils (Du et al., 2020). Continuous growth in phosphate fertilizer use has contributed to major increases in crop yields since the 1950s (Demay et al., 2023). However, the amount of readily available phosphorus is very low compared to the total amount of phosphorus in the soil (>80% is poorly available for plants) (MacDonald et al., 2011; Wu et al., 2022). Therefore, in many cases phosphorus fertilizers are needed to be used in order to meet crop requirements. Phosphorus availability to plants depends on various soil properties, most important of which are pH, $CaCO_3$, organic matter, and Al, Fe, and Mn oxides (Al-Rohily et al., 2013). There are two types of studies typically employed for estimating phosphorus availability: adsorption studies and the use of phosphorus extractants. These investigations have revealed that, for various reasons, phosphorus tends to be strongly retained by soils with alkaline and acidic pH values. In alkaline pH values, Phosphorus is bound by $CaCO_3$ (Naeem et al., 2013), while in acidic pH it is bound by soil oxides (Arai and Livi, 2013). Thus; the optimum pH range for maximum phosphorus availability is (6.0–7.0).

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*Corresponding author e-mail: mohamed.kotb@agr.cu.edu.eg
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The primary causes of Egypt's declining phosphorus availability are the high content of $CaCO_3$ in calcareous soils and high pH of the soil. The majority of the phosphorus that is administered in these circumstances is fixed by a precipitation reaction with calcium, which produces insoluble di- and octa-calcium phosphate complexes that are insoluble to plants (Khater 1995). Adsorption mechanisms including chemi-sorption and physio-sorption are the possible ways by which applied phosphorus gets fixed within the soil. Because of their strong surface interactions, small particle sizes, and natural abundance, iron (hydr) oxides are significant active components in environments (Navrotsky et al., 2008). The addition of phosphate to calcareous soils may cause a chain of events that progressively reduces the amount of phosphate that plants can utilize. The primary processes include phosphate precipitation as calcium phosphate minerals, adsorption onto calcium carbonate, iron (hydr) oxides, and clay minerals (Liu et al., 2012). Although distinguishing between the two processes is not always easy, it is widely accepted that phosphate can precipitate in large quantities or be retention by calcium carbonate at low concentrations (Liu et al., 2012). Adsorption can occur on a small number of sites at low phosphate concentrations, dependent on the Langmuir and Freundlich adsorption isotherms models (Yagi and Fukushi, 2012). Ca-compounds such di-calcium, brushite, octa-calcium phosphate, and hydroxyapatite precipitate at high concentrations following a short period of P-adsorption, according to Yagi and Fukushi (2012). In addition to calcium carbonate, the adsorption of iron (hydr) oxides in soils is intimately linked to the mobilization and adsorption of phosphate (Wang et al., 2024).

To improve the P acquisition efficiency of plants, an important step is to increase the concentration of available P in the rhizosphere (MacDonald et al., 2011). Humic acid (HA) as a natural organic matter, its presence can reduce P-adsorption, and promote the dissolution of inorganic P in soil (Lei et al., 2018). Humic acid (HA) can increase the P content in the soil, improve the effectiveness of P, and promote the migration of P fertilizers to the deeper layers of the soil (Xing et al., 2020). HA can increase P availability and uptake through known rates of calcium phosphate precipitation, forming P mates, which in turn improve crop growth response and yield. Also the pH, metal ions, ionic strength and the amount of HA in the soil affect the P release process (Zhang et al., 2022). Through soil mineralization, sorption, or desorption of soil-bound phosphorus, the application of humic acids (HA) in agricultural soils may have a positive or negative impact on the amount of phosphorus available in the soil. Traditionally, the addition of HA can reduce the capacity of the soil colloids to adsorb P, thus increasing the release of P in soil solution, but also added HA can increase the adsorption site and increase the fixation or sorption of P to soil colloids, thus reducing the availability of P in soil solution and loss to the environment. Humic acids have a lot of carboxyl, hydroxyl, and negative charge groups that compete fiercely for the phosphorus adsorption sites (Shen et al. 2011). Numerous studies have shown that organic substances can increase soil available phosphorus and the phosphorus activation coefficient in P-fixing soils by decreasing the strength of P-adsorption and its maximum buffering capacity and, to some extent, increasing P-desorption (Yang et al., 2019). The aim of the current study was to investigate the competitive sorption of phosphate and humic acid in calcareous soils.

2. Materials and Methods

2.1. Soil characteristics

Five soil samples were collected with different $CaCO_3$ contents (10.6%, 22.1%, 31.7% 42.5% and 51.3%, hereafter referred to S_1, S_2, S_3 S_4 and S_5, respectively), to represent the calcareous soils of Egypt, Locations for soil sample are displayed in Table 1 and Figure 1. Following air drying, crushing, sieving through a 2 mm screen, and homogenization, the samples were stored for examination to determine their physical and chemical characteristics.

2.2. Soil analyses

Following dispersion with sodium hexametaphosphate in accordance with the protocol outlined by IITA (1976), the hydrometer technique was used to determine the size distribution of the soil particles. Total calcium carbonate (T-$CaCO_3$) was determined using the volumetric calcimeter method (FAO, 2020), and active calcium carbonate (A-$CaCO_3$) fraction was determined by the back-titration method using 0.1 N ($KMnO_4$), after shaking the soil with 0.2 N $(NH_4)_2C_2O_4$ solution as described by (Bashour and Sayegh 2007). The pH in the suspension of (1: 2.5; soil: water) was measured using a combination pH electrode, and the electrical conductivity (EC) in the water extract (1: 2.5; soil: water) was investigated (Melero et al., 2007). The Walkley-Black (1934) wet oxidation method for identifying organic carbon was reported by Nelson and Sommers (1982). The cation exchange capacity was calculated using a modified version of Papaniclaou's (1976) methodology. An atomic absorption spectrophotometer (AAS) of the Perkin-Elmer model 1100B was used to measure the extracted Fe, Al, and Mn. Free oxides were identified using the dithionite-citrate technique (USSCS, 1972; Sherdrick and McKeague, 1975). Total and available phosphorus were determined using the method (Murphy and Riley, 1962). This method depends on extracting a portion of the phosphorus present in the soil and available for absorption by the plant using a sodium bicarbonate solution at pH=8.2, then the extracted phosphorus is estimated by the colorimetric method by treating the extract with an ammonium molybdate solution in an acidic medium, where a complex compound of ammonium molybdate phosphate is formed, which is reduced by ascorbic acid in the presence of antimony.

Table 1. The coordinates of the soil sampling locations in the studied areas using GPS.

Locations of soil samples	Coordinates		Location	Governorate
	E (Longitude)	N(Latitude)		
S_1	33°42'24.68"E	31° 6'21.89"N	Al-Sabil Village	North Sinai
S_2	30° 7'41.78"E	30°35'47.01"N	Shagaa Village	Beheira
S_3	29°38'3.70"E	30°50'54.45"N	Ezbet Mohamed Farid	Alexandira
S_4	29°54'1.94"E	30°53'32.36"N	El-Iman Village	Beheira
S_5	29°45'41.43"E	30°59'9.87"N	Nagaa Abou Bisisah	Alexandira

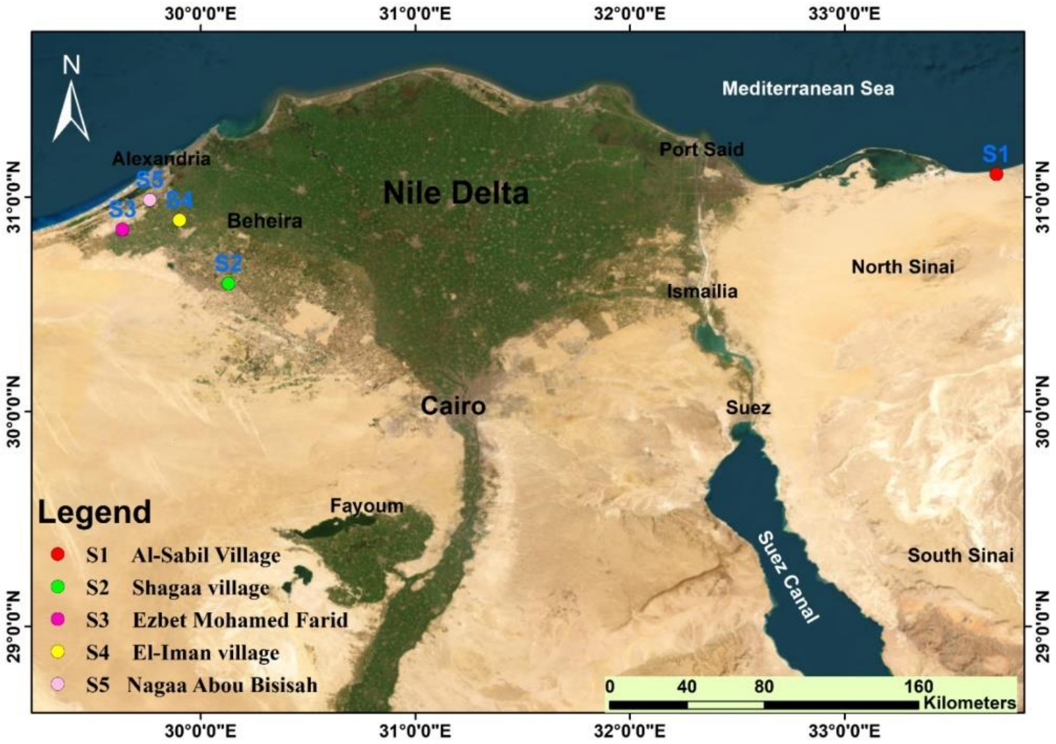

Fig. 1. Soil samples locations in Egypt.

2.3. Extraction of humic acid (HA) and characterization

The International Humic Substances Society's recommended procedure (Swift, 1996) was followed in order to extract and purify the humic acid (HA) from an animal compost (SEKEM Egypt Company) using a 0.5 mol L^{-1} NaOH solution. After dissolving HA in 0.05 mol L^{-1} $NaHCO_3$, the E_4/E_6 ratio of the HA sample was found to be 4.5. According to Reddy et al., (2014), the absorbance of the C chemical groups in HA was then measured at 465 and 665 nm, respectively, using a UV-visible spectrophotometer. HA fraction is usually assigned to E_4/E_6 ratio values less than or equal to 5, whereas fulvic acid is usually associated with values larger than 5 (Reddy et al., 2014). After the purification of HA, the Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra of HA separates measurements was made with a JesCo FTS 460^+ single beam. We used the KBr pellet technique (2 mg sample in 150 mg KBr), (Capriel et al., 1992; Celi et al., 1997), to obtain absorption spectra of HA fraction (range of wave number 3900-400 cm^{-1}); Spectra bands were obtained with resolution ($1cm^{-1}$).

2.4. Phosphate adsorption Isotherms

A duplicate of Five grams of soil samples was weighed into polyethylene centrifuge tubes, the soil samples were suspended in 50 ml of 0.02 M KCl solution, containing various phosphorous concentrations (0.5, 1.0, 2.5, 5.0, 10.0, 20.0, and 40.0 mg P l^{-1}) prepared from KH_2PO_4 salt, the suspensions were equilibrated for 24 hrs, At the end of the equilibration time, the suspensions were centrifuged, filtrated and P determined (Murphy and Riley, 1962). Phosphorus adsorption isotherm was determined for investigated soils at their native pH values. The amount of adsorbed P (A_e, mg kg^{-1}) was calculated using the following Equation:

$$\mathbf{A_e = [(C_i - C_e) \times v] \div m}$$

Where: C_i: The P initial concentration (mg l^{-1}); C_e: The concentration of P in solution at the equilibrium condition (mg l^{-1}); m: The mass of soil (kg), and v: The volume of the added P solution (l). The relationship between the adsorbed phosphorous and phosphorous in the equilibrium solution was described using the Langmuir and Freundlic modeles, The Langmuir isotherm model can be written in the following linear formula:

$$\mathbf{C_e/Q_e = 1/bQ_m + C_e/Q_m}$$

Where: C_e: concentration of P in soil solution at equilibrium (mg l^{-1}); Q_e: amount of P adsorbed per unit mass of soil (mg kg^{-1}); Q_m: maximum phosphorous adsorption (mg kg^{-1}); b: the Langmuir constant related to the energy of adsorption (L mg^{-1}), under the given experimental conditions. The Freundlich isotherm model can be written in the following linear formula:

$$\mathbf{Log\ Q_e = log\ K_F + 1/n\ log\ C_e}$$

C_e: the equilibrium concentration of P (mg L^{-1}); K_F: the Freundlich adsorption isotherm constant (mg kg^{-1}) that indicates the adsorption capacity of the adsorbent; n: the Freundlich adsorption isotherm constant.

2.5. Competitive sorption of P and HA Experiments (order of addition)

Three experiments have been carried out to predict the amount of P adsorbed on soils as affected by of HA (2.5 g kg^{-1} soil), amounts of P added (5, 10, 25, 50, 100, 200, and 400 mg P kg^{-1}), and order of P and HA additions. The order of addition were (i) P before humic acid (P/HA), (ii) P together humic acid (P+HA), and (iii) P after humic acid (HA/P). These experiments were performed at the natural pH values of the soils, a constant background of 0.02 M KCl, and a solid:solution ratio of 1:10. The steps of this experiment are explained as follows:

2.5.1. Phosphate Introduced before humic acid

(i) P before humic acid (P/HA), Five grams of soil samples were equilibrated for 24 hrs, with phosphorus solutions (KH_2PO_4 dissolved in 0.02 M KCl) containing (0.5, 1.0, 2.5, 50.0, 10.0, 20.0, and 40.0 mg P l^{-1}). After phosphate adsorption, the suspensions were equilibrated with humic acid (2.5 g kg^{-1} soil). The suspensions were shaken for another period of 24 hrs. The final suspensions (50 ml) were centrifuged, filtrated and P determined.

2.5.2. Phosphate Introduced together with humic acid

(ii) P together humic acid (P+HA), Fifty milliliters solutions of 0.02 M KCl containing both phosphorus and humic acid were added to 5 g soil samples. The suspensions were centrifuged, filtrated and P determined.

2.5.3. Phosphate Introduced after humic acid

(iii) P after humic acid (HA/P), Five grams of soil samples were equilibrated for 24 hrs, with humic acid (2.5 g kg^{-1} soil) in a 0.02 M KCl solution. Then the different concentrations of phosphate solutions containing (0.5, 1.0, 2.5, 50.0, 10.0, 20.0, and 40.0 mg P l^{-1}) were added to the soil suspensions. The soil suspensions were then equilibrated for another 24 hrs. The final suspensions (50 ml) were centrifuged, filtrated and phosphorus determined.

In all experiments, two drops of chloroform were initially added to inhibit microbial activity. Humic acid had to be precipitated by the addition of three drops of a concentrated HCl to 10 ml of the supernatant liquid and separated by centrifugation to give a clear solution. At the end of the reaction period, the suspensions were centrifuged at 5000 r.p.m. for 15 min and filtered. Then, Phosphorus was determined in the supernatant, spectrophotometrically by the Troug and Meyer method (Jackson, 1973). The amounts of adsorbed-P were calculated as mg P kg^{-1} soil from the difference between the initial and final concentrations of phosphorous in solutions (Violant et al., 1996).

2.6. Statistical analyses

Costat software was applied to analyze the collected data by means of analysis of variance (ANOVA). The treatment effects on the means of adsorbed phosphorus (adsorbed-P) for the order of phosphorus (P) and humic acid (HA) addition, significant at P=0.05, were compared using the Least Significant Difference (LSD).

3. Results

3.1. Soil characteristics

Table 2 shows Selected physical and chemical characteristics of the studied soils. The $CaCO_3$ content was significantly different between soils and varied between 10.55% (S_1) and 51.33% (S_5). Calcareous soils were neutral; to slightly alkaline, and low in EC values ranged from 1.22-1.88 dS m^{-1}. The pH of the soils ranged from 7.62 (S_1) to 7.89 (S_5), Organic matter (OM) and available P (AP) contents of this soil were low; OM varied from fro 19.5 (S_1) to 10.5 g kg^{-1} (S_5), while AP varied from 7.68.5 (S_1) to 18.4 mg kg^{-1} (S_5). The S_5 had the highest value of amorphous material (AM), (22.2 g kg^{-1}) and S_1 had the lowest value (10.5 g kg^{-1}) of amorphous material. The cation exchange capacity (CEC) varied from low (10.5 Cmol$_c$ kg^{-1}) in the S_1 to high (25.8 Cmol$_c$ kg^{-1}) in the S_5.

Table 2. Characteristics of the studied soil samples.

Soils	Property											
	pH	EC	Sand	Silt	Clay	OM	T-$CaCO_3$	A-$CaCO_3$	AM	TP	AP	CEC
	at 25°C	(dS m^{-1})	(g kg^{-1})							(mg kg^{-1})		(Cmol$_c$ kg^{-1})
S_1	7.62	1.22	758.8	115.1	126.1	19.5	105.5	70.6	10.5	120.6	8.5	10.5
S_2	7.55	1.56	712.7	132.4	155.2	15.2	221.1	80.7	12.3	150.4	10.6	11.6
S_3	7.85	1.10	573.7	203.2	223.1	14.1	316.5	95.8	15.7	230.5	12.2	14.2
S_4	7.69	1.62	521.8	221.7	256.5	13.2	424.6	105.4	18.5	270.3	15.3	17.5
S_5	7.89	1.88	387.7	257.8	354.5	10.5	513.3	120.5	22.2	390.8	18.4	25.8

Abbreviations: S_1: Al-Sabil Village (North Sinai Governorate); S_2: Shagaa Village (Beheira Governorate); S_3: Ezbet Mohamed Farid (Alexandira Governorate); S_4: El-Iman Village (Beheira Governorate); S_5: Nagaa Abou Bisisah (Alexandira Governorate); pH: Soil Acidity (Soil:water suspention 1:2.5); EC: Electrical Conductivity (Soil:water extract 1:2.5); ; CEC: Cation Exchange Capacity; OM: Organic Matter; AM: Amorphous material; T-$CaCO_3$: Total Calcium Carbonate; A-$CaCO_3$: Active Calcium Carbonate TP: Total Phosphorous; AP: Available Phosphorous.

3.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra of HA separates

The ATR-FTIR spectra of HA separated from animal manure compost are shown in Figure 2; IR bands were assigned in accordance with Stevenson (1994). The absorption bands from 3400 to 3200 cm^{-1}, with a peak at 3391 cm^{-1}, are assigned as OH groups, Phenol and alcohol; 2920 and 2851 cm^{-1} band for aliphatic CH stretching; 1615-1648 cm^{-1} for C=O stretching of COOH, The aromatic structure of C=C was identified at the 1570 cm^{-1} band and C-CH_3 groups at 1480 cm^{-1}. Further; the strong bending vibration of hydroxyl and carboxyl groups were recorded at absorption bands 1032 and 1103 cm^{-1}.

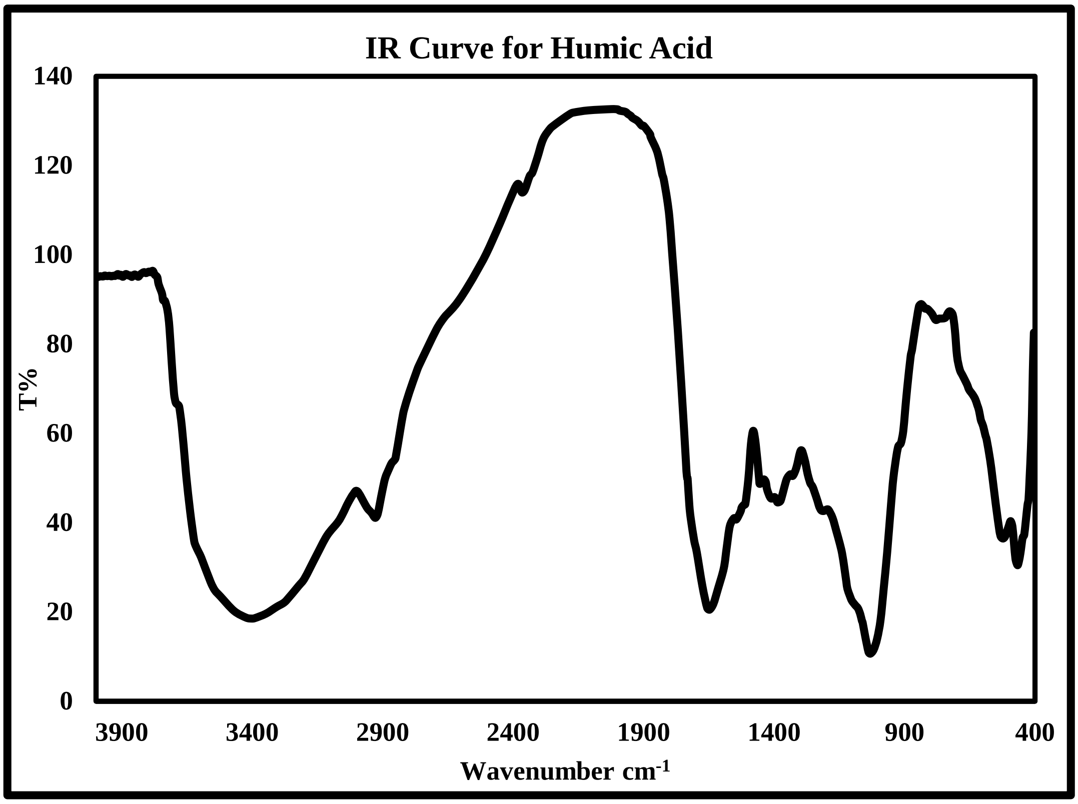

Fig. 2. ATR-FTIR spectrum and the main organic chemical groups recorded, for the humic acid sample (HA) extracted from animal manure compost.

3.3. P-adsorption isotherm and parameters

Phosphate adsorption isotherm was investigated for soil samples having different total and active $CaCO_3$. The adsorption isotherms were conducted at the natural pH values of the soils, and initial phosphorus concentrations of (0.5, 1.0, 2.5, 50.0, 10.0, 20.0, and 40.0 mg P l^{-1}). The P-adsorption isotherm of the soil samples was described mathematically using the Langmuir and Freundlich adsorption isotherms as summarized in Figures (3, 4 and 7). The adsorption data obtained for the studied soils were fitted significantly to the Langmuir and Freundlich models, based on its coefficient of determination value (R^2>0.82), the results also demonstrated good agreement with the Freundlich and Langmuir isotherms models (Tables 3 and 5). However, Freundlich isotherms described these data better than the Langmuir isotherms (R^2=0.821-0.930), due to their greater R^2 values (0.992-0.997). Figure 3 showed the P-adsorption isotherm which relates amount of P-adsorbed vs. concentration of final soluble P in soil solution at equilibrium. According to the results, when the concentration of phosphorus in the equilibrium solution (filtrate) increased, the amount of phosphorus absorbed also increased. For soil samples at any given final phosphorus concentration, the highest phosphorus absorption value was recorded in Nagaa Abou Bisisah (S_5) soil sample, and the lowest value in Al-Sabil Village (S_1) soil sample.

Figure 4 shows the recalculated P-adsorption data in the linear form of the Langmuir model. Langmuir constants for the examined soils were displayed in Table 3. The statistical correlation coefficient of determination (R^2) for C_e/Q_e versus C_e was significant for all the investigated soil samples and ranged from 0.821 to 0.930. This indicated that P-adsorption data were satisfactorily described by the linearized Langmuir model. The obtained data (Table 3) showed that maximum P-adsorbed was increased by increasing clay, total and active $CaCO_3$. The calculated maximum P-adsorption (Q_m) varied widely among the tested soils and ranged from 500 to 625 mg P kg^{-1} soil. The lowest value was reported for Al-Sabil Village (S_1) soil sample, whereas, the highest one was reported for Nagaa Abou Bisisah (S_5) soil sample. The bonding energy coefficients (b) of adsorbed phosphorus for the studied soils ranged from 0.010 to 0.017 (l mg^{-1}). The lowest value was reported for Al-Sabil Village (S_1) soil sample, whereas, the greatest value was recorded for Nagaa Abou Bisisah (S_5) soil sample.

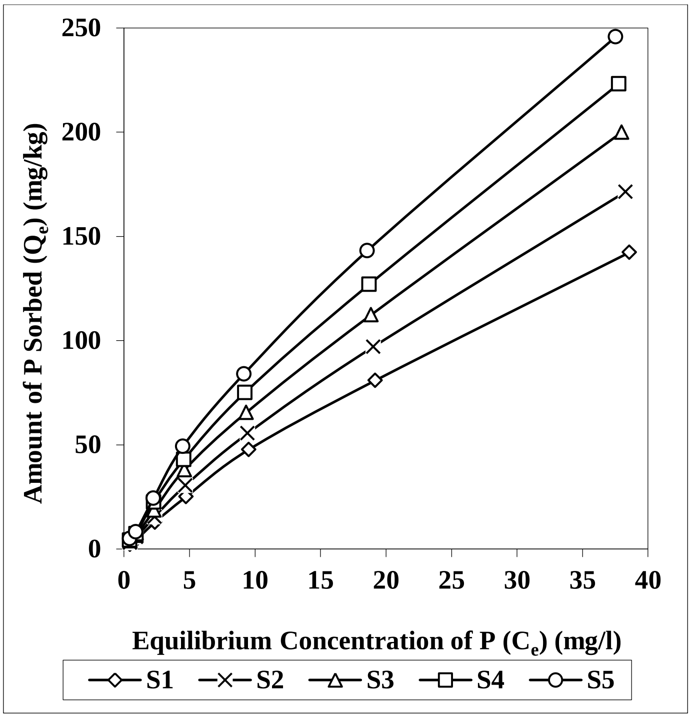

Fig. 3. Langmuir adsorption isotherms of P in the studied soils.

Abbreviations: S_1: Al-Sabil Village (North Sinai Governorate); S_2: Shagaa Village (Beheira Governorate); S_3: Ezbet Mohamed Farid (Alexandira Governorate); S_4: El-Iman Village (Beheira Governorate); S_5: Nagaa Abou Bisisah (Alexandira Governorate).

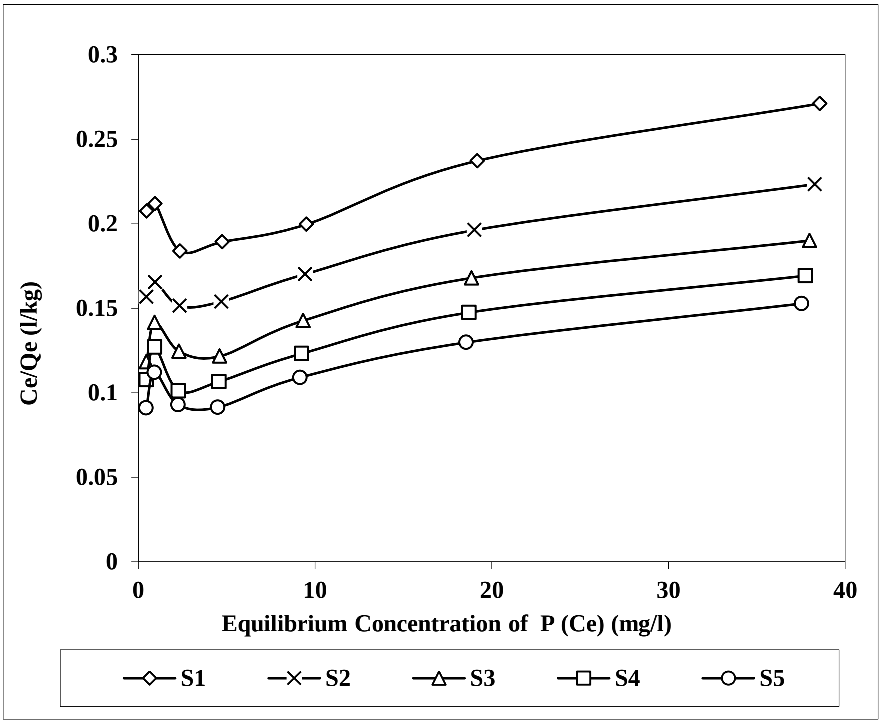

Fig. 4. Linear Langmuir model of P-adsorption for soil samples.

Abbreviations: S_1: Al-Sabil Village (North Sinai Governorate); S_2: Shagaa Village (Beheira Governorate); S_3: Ezbet Mohamed Farid (Alexandira Governorate); S_4: El-Iman Village (Beheira Governorate); S_5: Nagaa Abou Bisisah (Alexandira Governorate).

Table 3. Langmuir constant and coefficient of determination (R^2) for phosphate adsorption of the investigated soils.

Soil Samples	Q_m (mg kg^{-1})	b (L mg^{-1})	R^2
S_1	500.00	0.010	0.821
S_2	526.32	0.012	0.930
S_3	555.56	0.014	0.884
S_4	588.24	0.016	0.840
S_5	625.00	0.017	0.862

Abbreviations: S_1: Al-Sabil Village (North Sinai Governorate); S_2: Shagaa Village (Beheira Governorate); S_3: Ezbet Mohamed Farid (Alexandira Governorate); S_4: El-Iman Village (Beheira Governorate); S_5: Nagaa Abou Bisisah (Alexandira Governorate); (Q_m): Langmuir isotherm adsorption capacity (maximum phosphate adsorption); b: enthalpy related adsorption constant or The bonding energy coefficients.

The results show that calcium carbonate content positively affects the phosphorus bond energy to a large extent (R^2=0.99), (Figure 5). A highly significant and positive correlation was obtained between the maximum P-adsorption and $CaCO_3$% of the investigated samples (R^2=0.99), (Figure 6). The creation of the stable tri-Ca phosphate may be the reason for the highest P-adsorption's positive and substantial correlation with clay, AM, total-, and active-$CaCO_3$ (r=0.97, 0.91, 0.95, and 0.95, respectively) in Table 4.

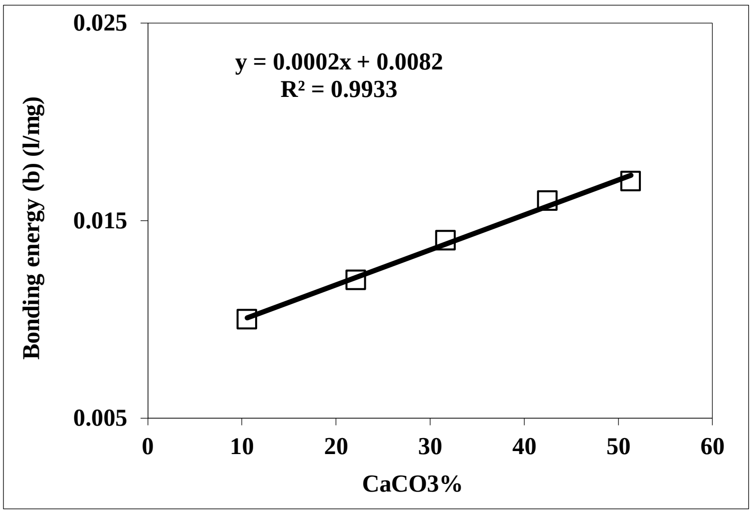

Fig. 5. Relation between the bonding energy (b) and content of $CaCO_3$% of the studied soil samples.

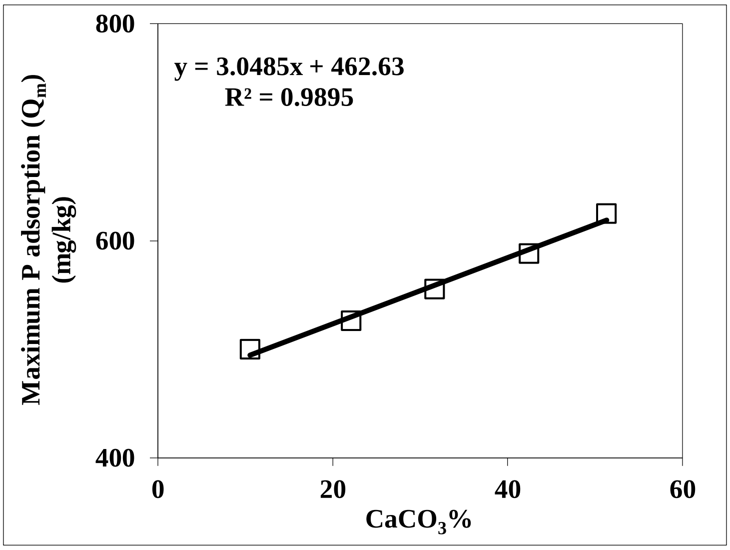

Fig. 6. Relation between the maximum P adsorption (Q_m) and content of $CaCO_3$% of the studied soil samples.

Table 4. Statistical correlation between selected soil chemical characteristics and both the Langmuir and Freundlich adsorption isotherms parameters.

Parameters	Q_m	b	n	K_f	pH	Clay	OM	T-$CaCO_3$	A-$CaCO_3$	AM	CEC
Q_m	1.00										
b	0.99	1.00									
n	0.94	0.97	1.00								
K_f	0.99	0.99	0.97	1.00							
pH	0.74	0.71	0.65	0.77	1.00						
Clay	0.99	0.96	0.91	0.98	0.81	1.00					
OM	-0.95	-0.95	-0.99	-0.96	-0.68	-0.93	1.00				
T-$CaCO_3$	0.99	1.00	0.97	1.00	0.72	0.97	-0.97	1.00			
A-$CaCO_3$	1.00	0.99	0.95	1.00	0.78	0.99	-0.95	0.99	1.00		
AM	1.00	0.98	0.93	0.99	0.77	0.99	-0.94	0.99	1.00	1.00	
CEC	0.96	0.90	0.84	0.93	0.75	0.98	-0.88	0.93	0.95	0.96	1.00

Abbreviations: (Q_m): Langmuir isotherm adsorption capacity (maximum phosphate adsorption); b: enthalpy related adsorption constant or The bonding energy coefficients; n: adsorption intensity constant; K_f: adsorption capacity constant or (distribution coefficient) (mg kg^{-1}); pH: Soil Acidity; OM: Organic Matter; T-$CaCO_3$: Total Calcium Carbonate; A-$CaCO_3$: Active Calcium Carbonate; AM: Amorphous material; CEC: Cation Exchange Capacity.

Data of P-adsorption was recalculated and represented in Figure 7 according to the linear form of Freundlich model; Table 5 showed Freundlich constants for the studied soils. The statistical correlation coefficient of determination (R^2) for log Q_e versus log C_e was significant for all the investigated soil samples and ranged from 0.992 to 0.997; this indicated that P-adsorption data were satisfactorily described by the linearized Freundlich model. The adsorption intensity constant (n) of adsorbed phosphorus for the studied soils ranged from 1.05 to 1.11. The Freundlich constant n is a measure of the kind of adsorption isotherm that takes place, According to Boparai and O'Carroll (2011), a chemisorption type is indicated by the homogeneous adsorption sites and strong affinity between the adsorbent and the adsorbate when value n>1. In this study, the least value were reported for Al-Sabil Village (S_1) soil sample, whereas, the greatest value was recorded for Nagaa Abou Bisisah (S_5) soil sample. The results show that calcium carbonate content positively affects the adsorption intensity constant (n) to a large extent (R^2=0.94), (Figure 8). Because K_F and the adsorbent's adsorption capacity are linearly correlated, the higher this constant, the higher the adsorption capacity. The calculated adsorption capacity constant or distribution coefficient (K_f) varied widely among the tested soils and ranged from 5.13 to 10.47 mg P kg^{-1} soil. The lowest value was reported for Al-Sabil Village (S_1) soil sample, whereas, the highest one was reported for Nagaa Abou Bisisah (S_5) soil sample. A highly significant and positive correlation was obtained between the adsorption capacity constant (K_f) and $CaCO_3$% of the studied samples (R^2=0.99), (Figure 9). The statistical relationship between chosen soil chemical characteristics and the parameters of the Freundlich and Langmuir adsorption isotherms was shown in Table (4). The Clay, T-$CaCO_3$, A-$CaCO_3$, AM, and CEC of the soil samples has shown a strong positive correlation with Q_m (r=0.99, 0.99, 1.00, 1.00, and 0.96, respectively); b (r=0.96, 1.00, 0.99, 0.98, and 0.90, respectively); n (r=0.91, 0.97, 0.95, 0.93, and 0.84, respectively); and K_f (r=0.98, 1.00, 1.00, 0.99, and 0.93, respectively); while soil organic mattter (OM); was a strong negatively correlated with these adsorption parameters (r=-0.95, -0.95, -0.99, and -0.96, respectively), for (Q_m, b, n, and K_f, respectively).

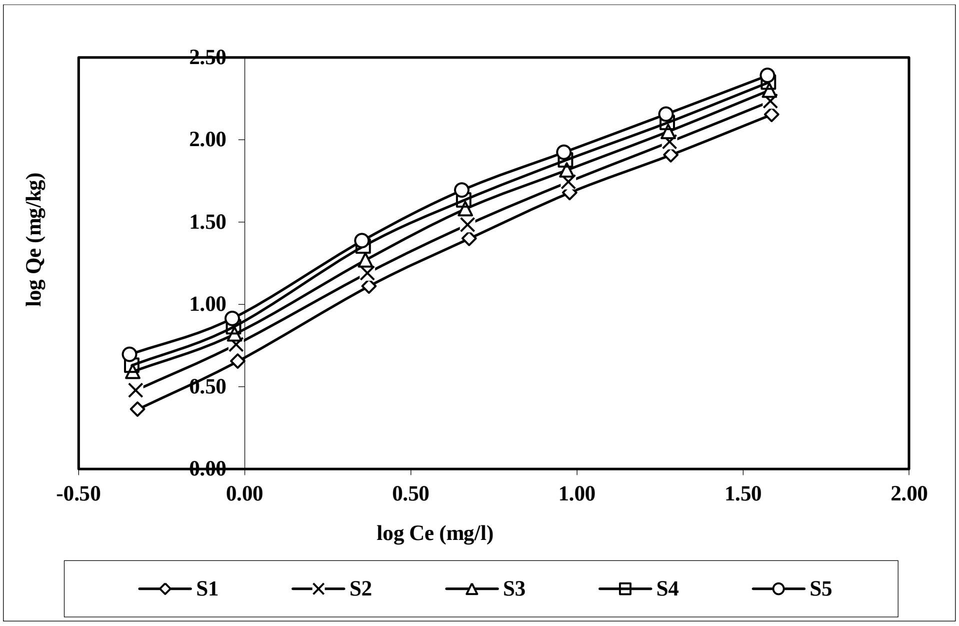

Fig.7. Linear Freundlich model of P-adsorption for soil sample.

Abbreviations: S_1: Al-Sabil Village (North Sinai Governorate); S_2: Shagaa Village (Beheira Governorate); S_3: Ezbet Mohamed Farid (Alexandira Governorate); S_4: El-Iman Village (Beheira Governorate); S_5: Nagaa Abou Bisisah (Alexandira Governorate).

Table 5. Freundlich constant and coefficient of determination (R^2) for phosphate adsorption of the investigated soils.

Soil Samples	n	K_f (mg kg^{-1})	R^2
S_1	1.05	5.13	0.995
S_2	1.08	6.46	0.997
S_3	1.09	8.13	0.995
S_4	1.10	9.12	0.993
S_5	1.11	10.47	0.992

Abbreviations: S_1: Al-Sabil Village (North Sinai Governorate); S_2: Shagaa Village (Beheira Governorate); S_3: Ezbet Mohamed Farid (Alexandira Governorate); S_4: El-Iman Village (Beheira Governorate); S_5: Nagaa Abou Bisisah (Alexandira Governorate); n: adsorption intensity constant; K_f: adsorption capacity constant or (distribution coefficient) (mg kg^{-1}).

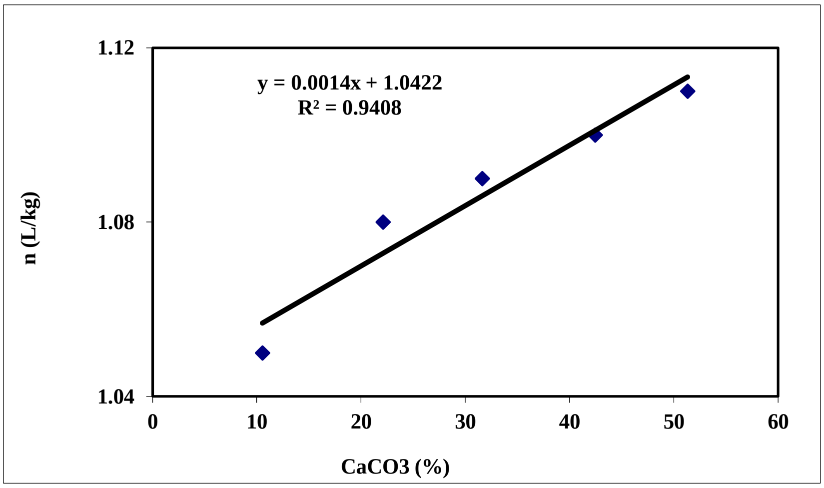

Fig. 8. Relation between the adsorption intensity constant (n) of adsorbed phosphorus and content of $CaCO_3$% of the studied soil samples.

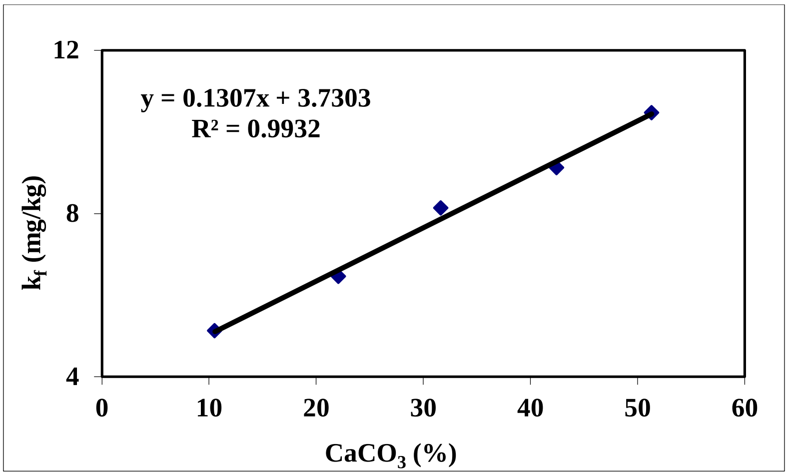

Fig. 9. Relation between the adsorption capacity constant or distribution coefficient (k_f) and content of $CaCO_3$% of the studied soil samples.

Table (6) shows the relationship between the effect of adding (2.5 g kg^{-1} soil) of humic acid (HA) to the soil and its effect on the amount of phosphorus absorbed on the surfaces of soil particles. From this table, it is clear that adding HA (2.5 g kg^{-1} soil) significantly reduced phosphorus absorption in all soil samples under study, according to the least significant difference analysis (LSD 0.05). This effect was particularly noticeable in the system in which phosphorus was added after humic acid (HA/P), which showed the lowest phosphorus absorption.

Table 6. Means of amount P adsorbed for the order addetion P and HA, as affected by Initial amount P added and their interaction.

Sorce	Means
order addetion P and HA	
P only	45.10 a
P/HA	36.49 b
P+HA	31.14 c
HA/P	26.68 d
LSD order addetion P and HA at 0.05	0.012
Initial amount P added	
5	1.90 g
10	3.95 f
25	10.05 e
50	18.60 d
100	34.99 c
200	61.16 b
400	113.30 a
LSD Initial amount P added at 0.05	0.015
Interaction of application order P and HA * Initial amount P added	
LSD order addetion P and HA * Initial amount P added at 0.05	0.031***

Note: Different letters in a column show a significant difference among means according to LSD test at $p \leq 0.05$. ***Significant at $p \leq 0.001$.

Figures (10-14) demonstrate how well humic acid reduces adsorbed P levels. The proportion of adsorbed P that the humic acid treated soils reduced compared to the untreated ones was calculated. It seems that reduction increased as the amount of P added increased in all the studied soils. The HA/P system was the most successful addition order in lowering adsorbed P in soils, particularly when 50 mg P kg^{-1} soil was supplied. When P was applied to soil samples at 5, 10, 25, 50, 100, 200, and 400 mg P kg^{-1} soil, the HA efficiency varied from 34.8-48.7, 22.4-39.4, 40.3-58.7, 46.6-61.5, 45.7-56.2, 40.7-52.1, and 39.1-53.2%, respectively. The percentage efficiency of HA (Figures 15-19) were computed using Deb and Datta's (1967) expression, as shown in the following equation, to assess its capacity to inhibit phosphate adsorption in the various systems:

$$[(1 - \text{P adsorbed in the presence of HA} \div \text{P adsorbed when applied alone})] \times 100$$

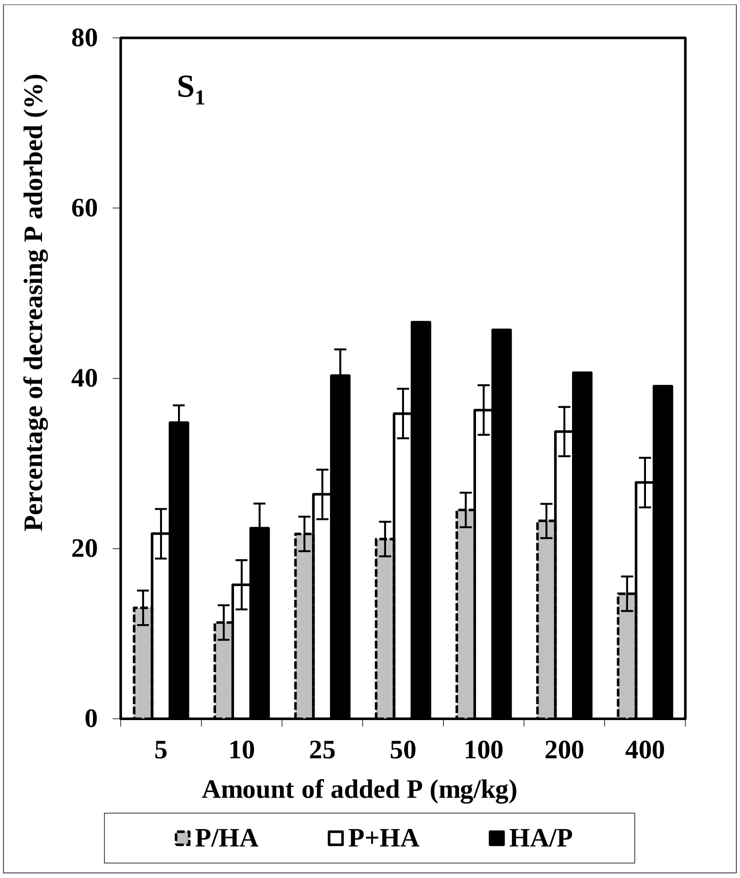

Fig. 10. Efficiency of HA in reducing P adsorbed by S_1 soil samples (S_1: Al-Sabil Village, North Sinai Governorate), as affected by the amount of added P and order of addition, Error bars are the standard error of three replicates.

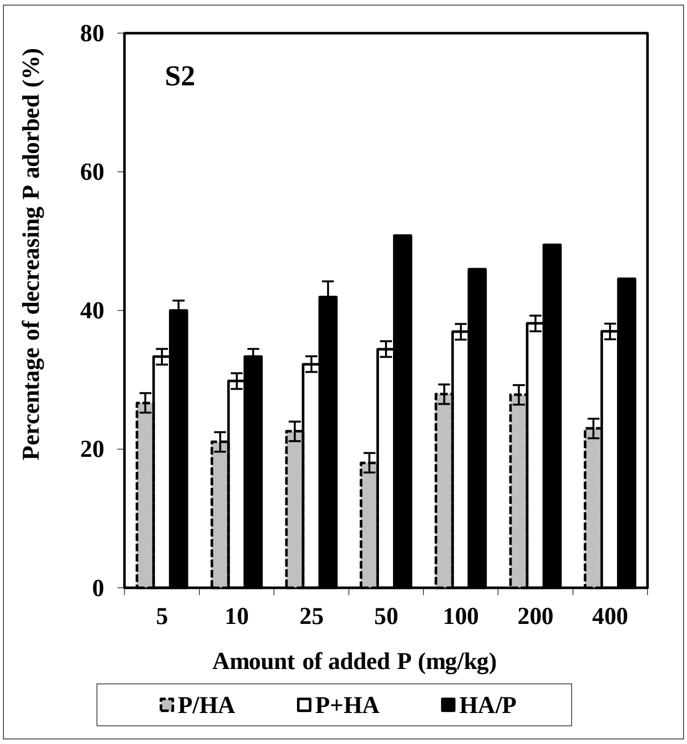

Fig. 11. Efficiency of HA in reducing P adsorbed by S_2 soil samples (S_2: Shagaa Village, Beheira Governorate), as affected by the amount of added P and order of addition, Error bars are the standard error of three replicates.

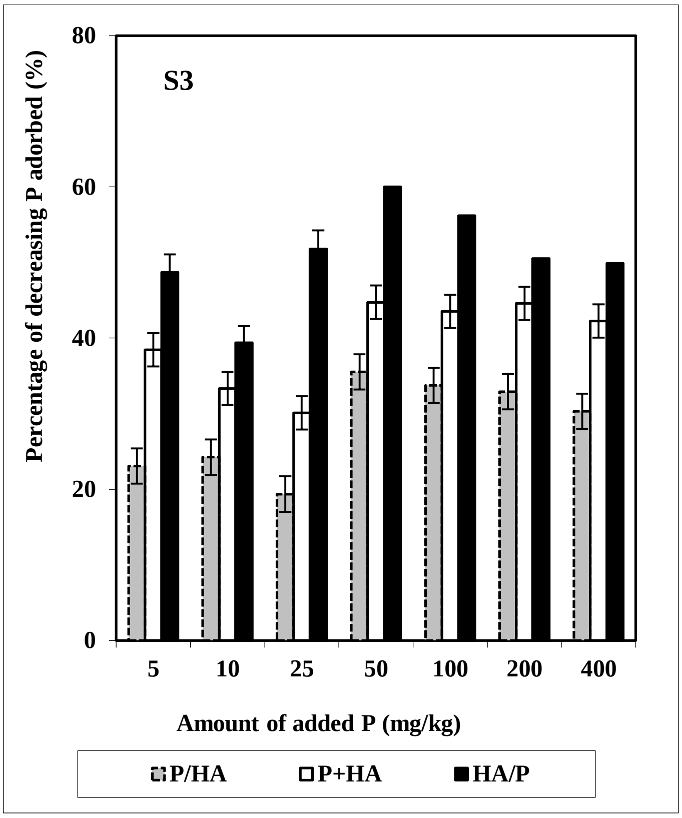

Fig. 12. Efficiency of HA in reducing P adsorbed by S_3 soil samples (S_3: Ezbet Mohamed Farid, Alexandira Governorate), as affected by the amount of added P and order of addition, Error bars are the standard error of three replicates.

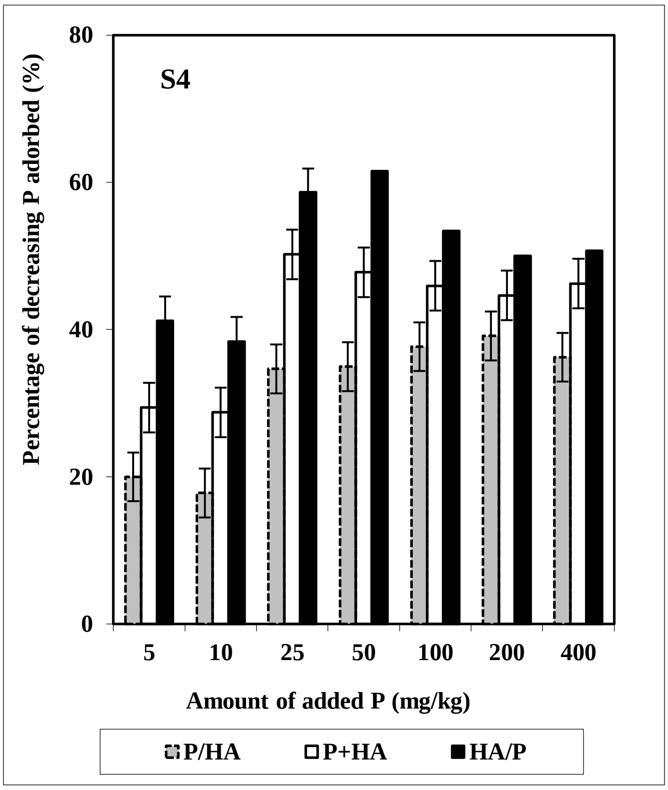

Fig. 13. Efficiency of HA in reducing P adsorbed by S_4 soil samples (S_4: El-Iman Village, Beheira Governorate), as affected by the amount of added P and order of addition, Error bars are the standard error of three replicates.

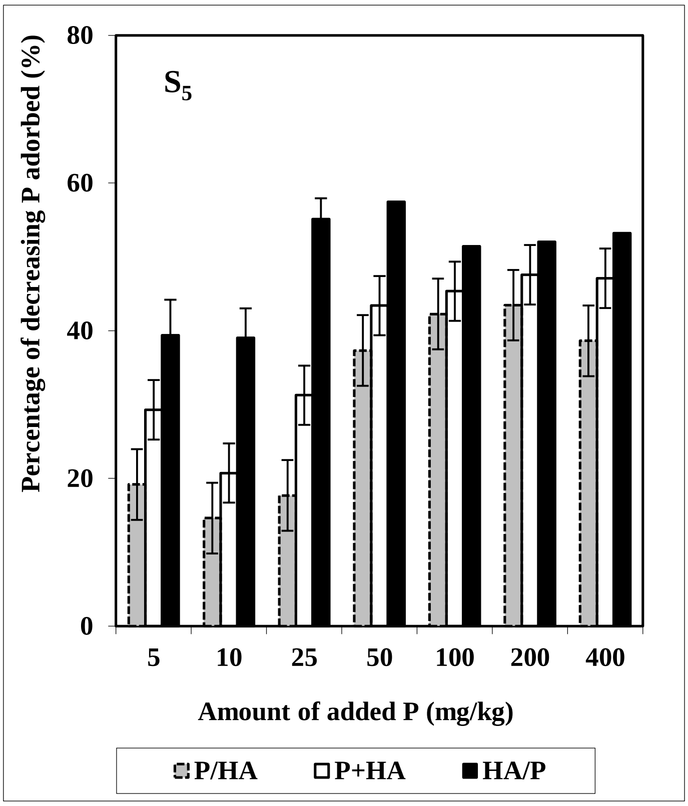

Fig. 14. Efficiency of HA in reducing P adsorbed by S_5 soil samples (S_5: Nagaa Abou Bisisah, Alexandira Governorate), as affected by the amount of added P and order of addition, Error bars are the standard error of three replicates.

4. Discussion

The characteristics of the investigated soil samples varied considerably (Table 2), which may influence phosphorus adsorption and mobility, and therefore phosphorus retention by the soils. In addition to that; the adsorption of phosphate on calcareous soil was studied as a function of concentration of the system. Similar increase in P-adsorption on calcium carbonate was observed elsewhere (Al-Rohily et al., 2013). These isotherms indicate that the P-adsorption increase by increasing its concentration in the solution. Based on the coefficient of determination (R^2) value, well-fitted models were found using the linearized versions of the Langmuir and Freundlich adsorption isotherm models. The amount of P adsorbed gradually changes, followed by a sudden increase as the P concentration increases. Two distinct processes could represent the interaction between soluble phosphorus and solid soil surfaces containing $CaCO_3$. The first process involved the chemisorption of a tiny quantity of phosphate, followed by the precipitation of calcium phosphate at greater phosphorus concentrations. This observation is consistent with that found by Khater (1995).

Figure (5) suggests that the relationship between soil $CaCO_3$ and phosphate adsorption may be influenced by the origin and type of $CaCO_3$. P-adsorption by soils varies widely with changes in soil physical and chemical characteristics (i.e., pH, texture, organic matter, and iron and aluminum oxides), as reported by Sanyal and De Datta (1991). From the obtained results, we note that the differences in the amount of P-adsorption between the studied soil samples are mainly related to the content of clay, amorphous material (AM), cation exchang capacity (CEC), total $CaCO_3$ (T-$CaCO_3$), and active $CaCO_3$ (A-$CaCO_3$) (Table 2). Thus, greater clay, AM and $CaCO_3$ contents in soils samples, explains the differential P-adsorption patterns between soils. Helal (1993) found that both soil $CaCO_3$ and Fe and Al (hydro) oxides represent the most reactive surfaces involved in P-adsorption in the soils of Egypt. According to El-Neklawy (1974), P-adsorbed in clay soil is readily released, whereas P-adsorbed in calcareous soil is challenging to recover. In soil solution, HA and phosphate usually exist together, and the humic ligand, which contains carboxyl groups, can compete with phosphate for binding to calcium ions. However, in competition, the existence of a rival and the manner in which the competitor is introduced into the system might alter the adsorption behavior. The effects of applying an initial concentration of 2.5 g kg^{-1} of HA on P-adsorption in soil samples are depicted in Figures (10-14). Combining HA and P (HA+P) in the solution resulted in a decrease in phosphate adsorption, suggesting that HA and P can both compete for similar surface locations and be adsorbed together on the surface of calcium carbonate particles.When HA was added before P

(HA+P) in the system, the decrease in P-adsorption was observed, as it is expected that HA will be adsorbed in a larger amount. The reason for decreasing P adsorption is that HA are a negatively charged molecule, and the steric effect and the increase in negative charge at the interface preventing the phosphate from approaching the surface Perassi and Borgnino (2014). Accordingly, we find that phosphate ions cannot displace HA from the surface. Contrary to what happened in the previous cases, we find that the P-adsorption process increases when phosphate is added first (P/HA) to the system. Where phosphate is absorbed first, and when HA is added second, the adsorption also occurs, but in a larger amount than without HA. It has an impact on the Ca-P compounds' saturation state as a report of Perassi and Borgnino (2014).

According to the findings of earlier studies, P-adsorption is strongly influenced by the order of application. When HA is applied first or together with phosphate, P-adsorption decreases. In contrast, when phosphate is applied first, adsorption increases. One possible explanation for this action is that humic acid inhibits the precipitation of Ca-P molecules. Results indicate that the presence of HA on the soils was able to restrict the sorption of phosphate especially at the higher amounts of added P and when HA introduced before it (HA/P) system. It could be postulated that the effectiveness of HA in competing with phosphate does not be exclusively in the occupation of adsorption sites by carboxyl group. Perhaps the more significant factor impeding phosphate adsorption is the adverse electrostatic field created around a precipitated humic acid molecule. In addition, part of adsorption energy of HA will be physical (Van der Waals) in nature which will not be involved in competition with phosphate (Sibanda and Young, 1986). Therefore, humified soil organic matter can drastically reduce the amount of P needed to keep the solution concentration at the level needed for crop growth. When humified organic matter is introduced before to phosphate fertilization, this effect is probably more noticeable. Hafiz et al., (2016), who tested the influence of fresh chicken, cow, and goat manure on P adsorption, found that soil amendment with manures reduced P adsorption capability. Furthermore the P sorption coefficient significantly decreased after manure treatment according to Yan et al., (2018).

Through the creation of a repulsive, negatively-charged, electrostatic field and competition for adsorption sites, this study showed that humic acid can dramatically decrease the adsorption of P on soil surfaces. Humic acid and calcium appear to form complexes when humic acid is added first. The study's findings highlighted how P and Ca form distinct complexes on the surface of $CaCO_3$, which dominated the interaction between HA and P adsorption on the soil surface. The P-adsorption capacity as influenced by P concentrations alone and in combination with humic acid was evaluated in calcareous soils. The application of HA causes these humic compounds to solubilize calcium phosphate and compete with phosphate ions in calcareous soils when humic acid is present. Additionally, it has been noted that manure-derived organic acids, sulfates, and fluorides compete with the adsorption site, reducing the adsorption capacity of manured soil phosphorous (Haynes and Mokolobate, 2001).

Dissolved organic carbon (DOC) compounds such as humic acid (HA) and fulvic acids (FA), which are released upon decomposition of OM, compete with added P for binding sites since both are negatively charged (Hunt et al., 2007). In the investigation of the effects of OM application on orthophosphate (O-P) adsorption, Yu et al., (2013) found that manure breakdown products such citrate and HA have a higher affinity for Al oxides, which is a significant sorbent for O-P. P-adsorption will therefore be decreased as a result of the competitive effect that organic matter addition will have on the binding sites between O-P and breakdown products on the soil surfaces. Its impact is less in soils with higher Al and Fe contents, such as heavily worn tropical soils like ferralsols. The added O-P discovers that the binding sites are already occupied since the DOC binds at the same binding sites of the soil complexes, or if both are added at the same time, the DOC has a higher chance of binding than the O-P (Yu et al., 2013).

In addition, the sorption of OM compounds to the soil mineral surface increases the negative charge or decreases the point of zero charge (PZC), thus inhibiting P sorption due to increased repulsion for incoming negatively charged anions such as phosphate (Guppy et al., 2005). It is observed that the sorption of OM can alter the surface charge of iron oxides and cause phosphates to be electrostatically repelled (Antelo et al., 2010). By enhancing physical soil characteristics like water-holding capacity, pH, aeration, and other soil attributes, OM addition can directly and indirectly affect the availability of P in highly worn soils. This can encourage plant development and greater use of soil P reserves. According to Fink et al., (2016), the change in the equilibrium of P between the soil's P pools also promotes increased P desorption from soil surfaces. Additionally, the additional OM might encourage microbial activity in the soil, which would raise organic P, decrease adsorbed inorganic P concentrations, and increase microbial P immobilization (Guppy et al., 2005). However, short-term soil pH increases caused by additional organic matter might reduce the availability of metal cations like Fe^{2+} and Al^{3+} by altering their solubility, which in turn reduces P-adsorption (Borggaard et al., 2005). Finally, higher amount of adsorbed P were reduced in the (HA/P) and (P+HA) systems than in the (P/HA) systems. Probably, the order of anion addition influenced differently the change in net surface charge of the surfaces with P and HA sorption, so that, different amounts of ligand were retained. The sequence of addition of P and HA may have an influence on how the organic anions are linked to the surfaces. Such observations could be taken as evidence of a deliberate strategy to improve phosphate nutrition for the grown plants.

5. Conclusions

To study the competitive sorption of phosphate and humic acid (HA) on calcareous soils with different CaCO3 contents, Three experiments have been carried out to predict the amount of P adsorbed on soils as affected by of HA (2.5 g kg−1 soil), amounts of P added (5, 10, 25, 50, 100, 200, and 400 mg P kg−1), and order of P and HA additions. The order of addition were (i) P before humic acid (P/HA), (ii) P together humic acid (P+HA), and (iii) P after humic acid (HA/P). The P-adsorption isotherm of the soil samples was described mathematically using the Langmuir and Freundlich adsorption isotherms. The results show that the adsorption data obtained for the studied soils were fitted significantly to the Langmuir and Freundlich models, based on its coefficient of determination value (R2>0.82), the results also demonstrated that adding HA (2.5 g kg−1 soil) significantly reduced phosphorus absorption in all soil samples under study, according to the least significant difference analysis (LSD 0.05). This effect was particularly noticeable in the system in which phosphorus was added after humic acid (HA/P), which showed the lowest phosphorus absorption. Because organic ligands have the ability to decrease P adsorption and promote P desorption in sols, combining inorganic P fertilizer with HA may boost phosphate availability and improve the efficiency of P fertilizer. The influence of HA on the environmental behavior of phosphate may involve the geochemical processes of phosphate in soils, as well as, soil characteristics. Further research is needed to define these processes and mechanisms.

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