تأثير أحماض الهيوميك على ادمصاص وتحرر الفوسفور في التربة الكلسية :
دراسة منحنيات الإدمصاص متساوية درجة الحرارة

Effect of Humic Acids on Phosphorus Sorption-Desorption in a Calcareous Soil: Parametric and Isotherms Study

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الملخص

نفـذ هـذا البحـث لدراسـة دور أحمـاض الهيوميـك (H) كعامـل مؤثـر علـى ادمصـاص - تحـرر الفوسـفور فـي التربـة الكلسـية، أُضيفت تراكيـز مختلفـة مـن حمـض الهيوميـك (0 - 1 - 1.6 - 2.4 - 4.8 مـغ H/غ تربـة)، واستخدمت معادلتـا لانغميـر (أحاديـة الطبقـة) وفرندلـش لتوصيـف منحنيـات ادمصـاص وتحـرر الفوسـفور. أوضحـت النتائـج أن زيـادة إضافـة الهيومـات H قـد أدت إلـى زيـادة ادمصـاص P فـي التربـة. أدت إضافـة هيومـات البوتاسـيوم بمعـدل H4 =4.8 مـغ/غ تربـة إلـى زيـادة مقـدرة التربـة لادمصـاص الفوسـفور، وتراوحـت القيـم العظمـى للادمصـاص Qm فـي التربـة الكلسـية بيـن 313 - 417 مـغ P/كـغ تربـة. مـع الإشـارة إلـى أن كميـة الفوسـفور المدمصـة كانـت أكثـر مـن 46 % مـن الفوسـفور المضـاف للتربـة الكلسـية. وذلـك عنـد معظـم معـدلات الهيومـات المضافـة، فـي حيـن انخفضـت كميـة الفوسـفور المتحـرر عنـد إضافـة الهيومـات بمعـدل 1.6 ≤ H مـغ H/غ تربـة، وعنـد مقارنـة منحنيـات الادمصـاص والتحـرر يتبيـن انخفـاض واضـح فـي كميـة الفوسـفور المتحـرر مـن الجـزء المدمـص.

الكلمات المفتاحية: أحماض الهيوميك، الفوسفور، الإدمصاص، التحرر، التربة الكلسية.

Abstract

This study was conducted to determine the role of humic acid (HA) as an important factor affecting the adsorption-desorption of soil P, deferent concentrations of humic acid (0 - 1 - 1.6 - 2.4 - 4.8 mg HA/g soil) were added to a calcareous soil, and both Langmuir (mono-layer) and Freundlich models were used to describing adsorption-desorption isotherm. The results indicated that increased HA led to increase adsorption P in the soil. The HA4 (4.8 mg.g^{-1}) had the highest P retention capacity, whereas the Langmuir sorption maximum values Q_m for calcareous soil were between 313 - 417 mg.kg^{-1}. Phosphorus adsorption by the calcareous soil was greater than 46% of the amount added. The P-desorption is low in the treatments HA$\geq$ 1.6 mg.g^{-1}, and the comparison of the sorption and desorption isotherms reveals a pronounced hysteresis, that is, the irreversibility of the sorption.

Keywords: Humic Acid, Phosphorus, Adsorption, Desorption, Calcareous Soil.

Introduction

Phosphorous (P) is one of the most abundant elements and is necessary for plant growth. Thus, it is an important component of fertilizer for crops grown in most regions (Weeks and Hettiarachchi, 2019). There is an increased use of P fertilizers with increasing food demands, leading towards the accumulation of P in soils associated with Fe, Al, and Ca. Thus, the turn chemically application of phosphate fertilizer involving a sustained enhancement of solubility and availability in soil is the key point to solve the phosphorus crisis, lastingly and world-wide (Weeks and Hettiarachchi, 2019).

Scientists are currently working to parse whether the commercial versions of humic substances reliably benefit to cropping systems and, if so, what the mechanism of action may be (Kleber and Lehmann, 2019). humic acid (HA) is the main source for adsorption sites in humic substances and contains various functional groups like carboxyl groups (COOH), alcoholic hydroxyl groups (OH), and phenolic hydroxyl groups (Lin *et al*., 2017). One common hypothesis is that the high cation exchange capacity associated with P and through complexation with Fe and Al in acid soils and Ca in calcareous soils. All this causes preventing precipitation of phosphate (Weeks and Hettiarachchi, 2019). In addition to these mechanisms, the HA adsorbed on soil mineral component can generate a repulsive negative electrostatic field and, due to its high molecular weight, may also promote a physical barrier at the mineral surface, which reduces the P affinity to soil colloids (Yan *et al*., 2013; Wang *et al*., 2016).

Degryse *et al*. (2013) concluded the previous mechanism to prevent fixation was likely not viable. Others have been unable to demonstrate the utility of this mechanism as well but results in some published studies suggest that humic substances or at least elevated levels of soil organic matter seem to increase P extractability (Guedes *et al*., 2016; Weeks and Hettiarachchi, 2019). It was also found that the P adsorption capacities and P-buffering capacity of soils were dependent on the type of organic fertilizer applied and the soil type (Rosa *et al*., 2018).

The efficiency by which the P is adsorbed depends on the supply of P to the soil, P desorption, and on the buffering capacity of the soil (Wang and Liang, 2014). P adsorption/desorption is equally important in terms of increasing the rate at which P can be used by plants. Therefore, a contradictory results for P adsorption/ desorption were obtained for different soils that seem to relate to the type and nature of the soil and organic matter added or present in the soil (Kleber and Lehmann, 2019). Othieno (1973) suggested that Humic acids can have a detrimental effect on P availability for plants. Thus, further elucidation of the relationships between humic acids and P in competitive sorption processes is necessary.

Several models have been developed to quantitatively describe the sorption isotherm, the most popular being the Langmuir and the Freundlich equations (Wang *et al*., 2016). These studies have highlighted that P sorption can be explained quite satisfactorily by using different isotherm equations, but that no single equation can be considered suitable for all soil types. Calcareous soils are widely spread in arid areas worldwide (Taalab *et al*., 2019). It has been estimated that these soils comprise more than 30% of the world's land. Little has been reported on the P sorption-desorption in calcareous soils amendment with different concentrations of humic acid. The optimum rate of humic substances to P availability in soils is not mentioned in the studies performed by Yan *et al* (2013). Therefore, the objectives of this study was to investigate the effect of HA concentrations on (1) P-adsorption isotherms described using Langmuir and Freundlich parameters in calcareous soil, and (2) studying the effect of different concentrations of humic acid on the desorption of P.

Materials and Methods

1. Study area and soil sample collection:

The soil was collected from the depth 0-30 cm, from Stkheres Agricultural Research Station, Lattakia with latitude 35°.33'02' N, 35°.52'58' E. Soil samples were air-dried and processed to pass 2 mm sieve prior to analysis. The soil properties are shown in Table 1.

Table 1: The soil properties.

Soil Particle Distribution (%)			soil texture	pH	OM	CaCO$_3$	Active lime	Olsen-P
Clay	Silt	Sand		1:2.5 Soil:water	——— % ———			mg P.kg^{-1}
38	18	44	Clay loamy	7.6	0.88	49.7	10.4	18.9

The humic acid (HA) used from a biochemical trade product **Powhumus[85]** (**Humintech-German biotech)**, contained negligible total P, Potassium Humates 80-85%, Particle size of Insol. Cont. <100 Microns, Solubility in water 100%, Bulk density ca. 0.55 kg/L, CEC 400-600 meq/100g, pH-Value 9-10.5 (data analysis as published by Humintech Co.).

2. Phosphate adsorption and desorption:

Adsorption isotherms were acquired using the batch equilibrium method as modified by (Yan *et al.*, 2013). 2.5 g soil was taken into polypropylene copolymer centrifuge tube, each receiving 25 mL of CaCl$_2$ solution (*0.01 mol.L$^{-1)}$* at pH 7.0.The CaCl$_2$ solutions containing P (as KH$_2$PO$_4$) at concentrations of 0, 5, 10, 20, 40, 60, 80 and 100 *mg L^{-1}*. Then, the same tubes received Humic acid at rates of (0 - 1 - 1.6 - 2.4 - 4.8 mg HA/g soil).

All treatments were performed in triplicate. Tubes were shaken in an end-over-end shaker at 120 oscillations per min at 25 ± 1 °C for 16 h to allow equilibrium to be reached and centrifuged at 3000 rpm for 10 min. Supernatants of each tube (equilibrium) were then filtered through Whatman No.42, and P concentration in the equilibrium solution was determined colorimetry (Murphy and Riley, 1962). The amount of P adsorbed was then calculated as the difference between the initial amount of P added and P remained in solution.

Treatment tubes were then washed with 25 mL alcohol (95%) by shaking for 1 hour, centrifuged, and the alcohol was discarded. This process was repeated three times to ensure the removal any un-adsorbed P left from the sorption study and in preparation for the desorption study.

A 25 mL of KCl solution (*0.01 mol.L$^{-1)}$* at pH 7.0 was then added, and tubes were shaken, centrifuged, and P was determined in the supernatant as described above. The P concentration in the solutions was defined as desorbed P.

3. P adsorption models:

Adsorption model can be described using the Langmuir monolayer equation (*Ce/Q = Ce/Q$_m$ +1/k$_l$Q$_m$*). The Freundlich linear equation (*Q = k$_f$Ce$^{1/n}$*), and the logarithmic form of the equation becomes (*LogQ$_e$ =LogK$_f$ +1/n.LogC$_e$*), where *Q* (mg.kg^{-1}) is the amount of P adsorbed on soil at the equilibrium P concentration *Ce* (mg.L^{-1}), *Q$_m$* (mg.kg^{-1}) is the maximum amount of P adsorbed to the soil, and *k$_l$* (L.mg^{-1}) is a constant related to the binding strength of P at the adsorption sites. *K$_f$* is the adsorption constant and n is a constant whose value varies between 0 and 1 (Wang *et al.*, 2016).

Desorption isotherms can be described using the Langmuir equation *(Ce/D = Ce/D$_m$ +1/k$_l$.D$_m$)* and the Freundlich equation *(D = k$_f$Ce$^{1/n}$)* where *D* (mg.kg^{-1}) is the amount of P desorbed from the soil at the equilibrium P concentration *Ce* (mg.L^{-1}), *k$_l$* (L.mg^{-1}) is a constant related to the desorbing strength, and *D$_m$* (mg.kg^{-1}) is the maximum amount of P desorbed. The percent P desorption (*D$_r$*) was calculated as fallow; Percent P desorbed *Dr =*

3. Statistical analysis:

The equilibrium of P-concentration for adsorption and desorption was analysed by analysis of variance (ANOVA) using SAS procedures (SAS Institute, 1999). Mean separation was then determined for variables at each P and HA concentration using the least significant difference (LSD) at "0.05" level of significance.

Results and Discussion

Adsorption characteristics:

1. P adsorption isotherms:

The P-adsorption isotherms with different concentration of HA are shown in Figure 1. The addition of HA increased the P-adsorption capacity of calcareous soil, but did not affect the basic shape of the adsorption isotherms, i.e. an initial rapid increase in adsorption followed by a gradual increase. The results indicate that P sorption increased rapidly as P concentration in equilibrium solution increased to 20 mg.L^{-1} but relatively slowly increased as P equilibrium solution concentration increased further, to 30 and then 76 mg.L^{-1}.
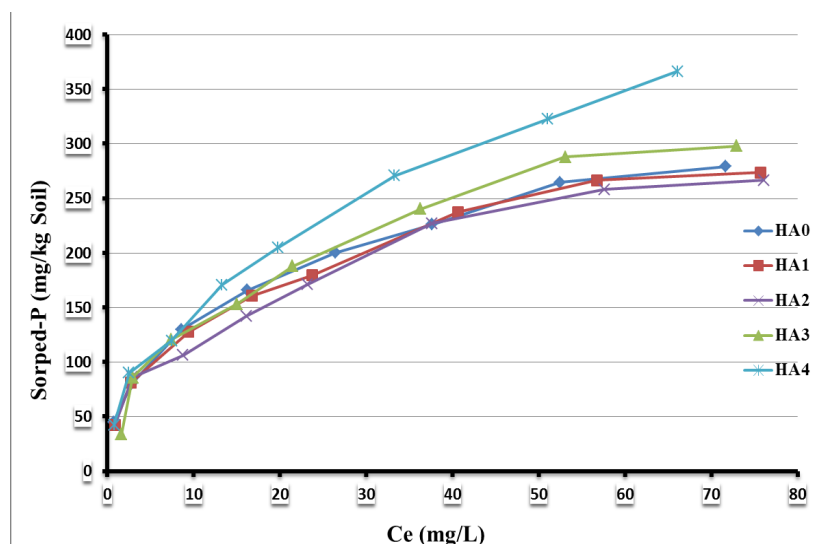

Figure 1. Phosphorus (P) sorption isotherms in soil with different humic Acid treatments (HA0=0, HA1=1, HA2=1.6, HA3=2.4, HA4= 4.8 mg HA/g soil).

The sorption curve was similar in shape for all treatments and is of type L. This is the common type for phosphorus sorption, which is characterized by high affinity at low equilibrium concentrations of P evident from the slope of the curve. The affinity decreases with increasing the concentration of P in the equilibrium solution (Wang and Liang, 2014). The amount of P-sorbed on the soil was varied with the difference of added HA, whereas the HA_4 (4.8 mg.g^{-1}) had the highest P retention capacity, and HA_3 had less adsorption P retention capacity.

The curve slope was nearly the same for all treatments at low P concentrations in the equilibrium solution. This would probably means that there was weak effect for humic acid. However, the effect of HA appeared at high concentrations of P in the equilibrium solution, whereas HA_3 and HA_4 showed high affinity and increased the amount of sorption-P. The adsorption affinity of P to soil estimated by slopes isotherms was very close to control when using low concentrations of humic acids (HA≤ 1.6 mg.g^{-1} soil). Despite the competition between phosphorus and Humic acid on adsorption sites, but it was less than the increase in adsorption sites caused by humic acid during the adsorption reaction. This may cause an increase in the total absorption capacity. The increased concentration of added HA led to an increase in sorption of P on soil by stimulation of adsorption sites on metal such as Al/Fe oxides or by forming ligand metal-HA-P (Kleber and Lehmann, 2019; Wang *et al.*, 2016).

This result might be due to the trend to the relatively stronger P-sorption capacities on calcareous soil with added HA. The addition of HA which has a low degree of mineralization would decrease competition for adsorption sites. In contrast, it might increase the number of adsorption sites in the soil, and hence increasing P adsorption. These results are in line with those obtained by Yan *et al*. (2013). Zhao et al. (2006) reported that the different P-sorption capacities of the soil from the different concentrations of HA were closely related to soil pH, and the soils with a pH > 6.0, the organic matter in the soil increased P-adsorption, whereas, for soils with a pH < 6.0, OM decreased P-adsorption. It is worth noting that humic acids may also act as P-sorbing surfaces in some circumstances and the reactions of metals with HA greatly increase P sorption thus may help alleviate problems associated with high P fixation through the slow mineralization of these complexes (Guppy *et al*., 2005).

2. P adsorption models:

The parameters and coefficients were calculated from Langmuir and Freundlich P-adsorption isotherms Table 2. The results indicate that equations of Langmuir and Freundlich are fitted well the P adsorption isotherms based on the R^2. The correlation coefficients of all the relationships are statistically significant. Either equation could, therefore, be used to describe the P adsorption characteristics of the soil with different HA contents, and are in agreement with other studies (Lin *et al*., 2017; Yan *et al*., 2013).

Table 2. Phosphate adsorption models for different HA treatments (means±standard deviation).

Treatments	Langmuir Equation			
	$Ce/Q = 1/Qm.Ce + 1/(Qm.K_l)$	Qm (mg.kg^{-1})	k_l (L.mg^{-1})	R^2
HA0	$Ce/Q = 0.0032C_e + 0.0337$	313 ± 6.5 C	0.098 ± 0.004 A	0.9788**
HA1	$Ce/Q = 0.0032 C_e + 0.0361$	313 ± 3.2 C	0.089 ± 0.001 A	0.9789**
HA2	$Ce/Q = 0.0033 C_e + 0.0413$	303 ± 3.2 C	0.082 ± 0.001 A	0.9682**
HA3	$Ce/Q = 0.0028 C_e + 0.0442$	357 ±8.5 B	0.066 ± 0.002 A	0.9813**
HA4	$Ce/Q = 0.0024 C_e + 0.0355$	417 ± 24.3 A	0.069 ± 0.002 A	0.9504**
LSD$_{0.05}$		41.21	0.08	
Treatments	Freundlich Equation			
	$LogQ = LogKf + 1/n.Log C$	$1/n$	K_f (mg.g^{-1})	R^2
HA0	$LogQ = 1.7347 + 0.3944.logC$	0.394 ± 0.042 C	5.67 ± 0.046 AB	0.9963**
HA1	$LogQ = 1.742 + 0.3818.logC$	0.381 ± 0.003 C	5.71 ± 0.019 A	0.994**
HA2	$LogQ = 1.7129 + 0.3862.logC$	0.386 ± 0.055 C	5.54 ± 0.063 B	0.9675**
HA3	$LogQ = 1.562 + 0.5225.logC$	0.522± 0.014 A	4.77 ± 0.031 C	0.935**
HA4	$LogQ = 1.7358 + 0.4517.logC$	0.452± 0.048 B	5.67 ± 0.048 AB	0.9834**
LSD$_{0.05}$		0.023	0.15	

Different letters within a column are significantly different at $P < 0.05$; K1, binding energy; Qm, adsorption maximum; R2, coefficient of determination; Kf and n are empirical constants, (HA0=0, HA1=1, HA2=1.6, HA3=2.4, HA4= 4.8 mg HA/g soil).

The Q_m values for calcareous soil were between $313 - 417$ mg.kg^{-1}. The addition of HA had a clear influence on Q_m, which significantly increased as applied HA ≥ 2.4 (HA$_3$) mg HA/g soil compared to other treatments, While the relationship was not statistically significant ($P < 0.05$) for the treatments HA$_0$, HA$_1$, and HA$_2$. The increase of HA added rates to the soil may favour P sorption through the formation of HA-cation-P complexes (Urrutia et al., 2014). This may prevent a linear decrease of Q_m, while adsorption of organic anions on soil colloid surfaces can increase P adsorption through interactions of phosphate with Ca^{+2}, reducing P -mobility and availability (Weng; Riemsdijk; Hiemstra, 2012). Thus, adding HA to calcareous soil can either decrease or increase P sorption, depending mainly on the HA rate added, exchangeable cation contents, and organic-cation-P complexes formed in soil.

It was indicated that the P storage capacity of the calcareous soil increased as the HA content increased (Zhou and Li, 2001). Yan *et al.* (2013) found that organic matter content does not directly affect the Q_m, and the addition of organic fertilizers to soils that have pH > 6 led to unstable changes in the Q_m. We speculate that several factors might have caused this phenomenon, including the composition of the introduced organic fertilizers, the soil incubation period, and the parent material of the soil. Further investigation is required to obtain a better understanding of the factors relating to this phenomenon. The Freundlich (K_f) and Langmuir sorption maximum (Q_m) parameters were found to correlate positively with total clay and non-carbonate clay content of soils (Zhou and Li, 2001), but not with the carbonated clay soils. This implies that the non-carbonate clays (such as Fe oxide, Al oxide, and Si clays) are the main surfaces for P sorption. On the contrary, total carbonate content appeared to have a negative influence on P sorption (Zhou and Li, 2001). Indeed, an indirect negative effect of total carbonate has been reported in other calcareous soils (Taalab *et al.*, 2019).

Desorption characteristics:

1. P desorption isotherms:

P desorption from the soil is considered to be the reverse of the adsorption process. Desorption is more important than adsorption because of the importance of immobilized P in the soil becoming available for reuse and also because of the environmental problems of released-P from soil (Wang and Liang, 2014). The amount of P desorbed from the soil samples, whether received humic acids or not, increased as solution P concentration increased (Figure 2). The HA content affected P desorption, the amounts of P desorbed was higher for the HA$_1$ soil samples than other treatments.

In contrast, adding higher concentration of humic acids (H ≥ 1.6 mg.g^{-1}) caused a negative effect and decreased the amount of P released to the soil. These results are consistent with the results of other studies (Rosa *et al.*, 2018). As of HA$_2$ concentration (1.6 mg.g-1), the HA has magnified its activity in the calcareous soil and promotes the opposite effect, contributing to P adsorption in the soil through the formation of HA-cation-P complexes, with a reduction in P desorption content.
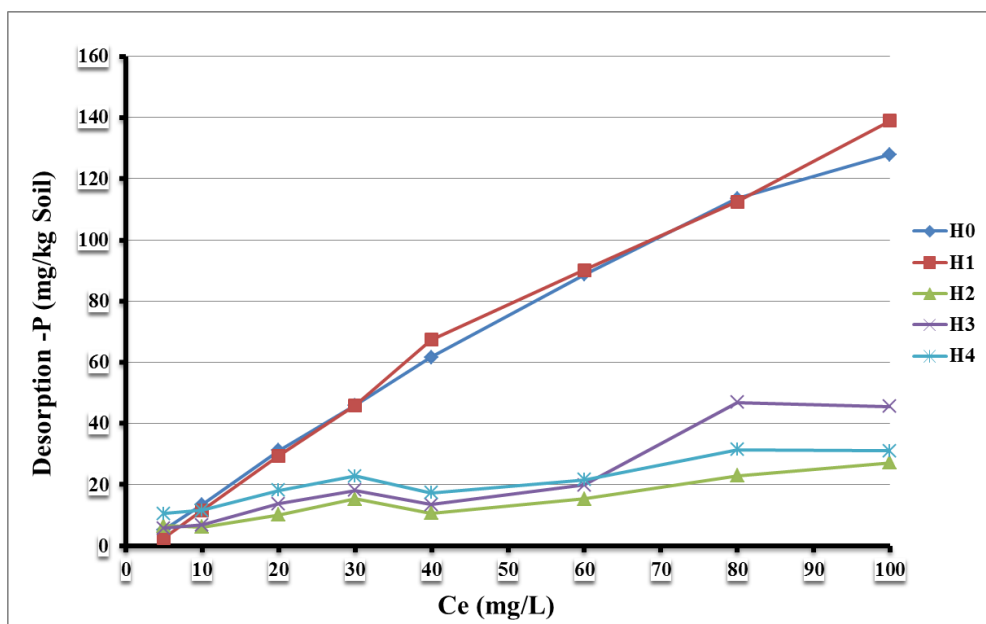
Figure 2. Phosphorus (P) desorption isotherms in soil with different humic acids treatments (HA0=0, HA1=1, HA2=1.6, HA3=2.4, HA4= 4.8 mg HA/g soil).

Phosphorus adsorption in this soil increased over HA concentration through associations with organic compounds, cation, and P, with variable reversibility of the complexes formed (Urrutia *et al*., 2014). This organic complexation with greater stability of P may have been the main factor that prevented the linear increase in extractable P contents at the highest concentrations of HA in calcareous soil. In short term interaction, the reversibility of the complex is expected to be low due to the greater availability of organic ligands in the medium over concentrations higher than (1.6 mg.g-1) of HA. The desorbed P contents are different in soils. Thus, plenty of studies indicated the difference of P buffering capacity, directly related to the properties of these soils, such as clay content (Rosa *et al*., 2018).

2. Desorption parameters

The Desorption of Langmuir and Freundlich equation was shown in Table.3. The maximum P desorption capacity (D_m), defined as the amount of P desorbed when the adsorbent was saturated with P and reflected the maximum amount of P supplied to the soil. The range D_m values for calcareous soil with and without receiving HA were (909 - 42.1 mg.kg-1).

Increasing HA content from (1.6 to 2.4 mg.g^{-1}) caused significant decrease of D_m, The desorption capacities were always lower than the maximum adsorption capacities for P (Table 2). The D_m was significantly higher ($P \leq 0.05$) in control sample where no HA added (HA_0 = 909 mg.kg-1) compared to samples received lower concentration of HA (HA_1 = 434 mg.kg-1). The Dm value was decreased while HA concentration increased, meaning that increasing the H content decreased the amount of P that desorbed and entered the soil solution.

Table 3. Parameters of phosphate desorption equations for different HA treatments (means ± standard deviation).

Treatments	Langmuir equation			Freundlich equation			
	$C/Q = 1/b.C + 1/kb$	$Dm\ mg.kg^{-1}$	R^2	$Log\ Q = Log\ K_f + 1/n\ Log\ C$	n	K_f	R^2
H0	C/Q = -0.0011.C + 0.1117	- 909 ± 87.5	0.5*	Log Q =0.9657+ 1.0304.log C	0.97 ± 0.001 A	2.63 ± 0.002 A	0.9999**
H1	C/Q = -0.0023.C + 0.1249	- 434.8 ± 41.4	0.3717*	Log Q =0.9525+ 1.0419.log C	0.95 ± 0.001 A	2.59 ± 0.003 B	0.9998**
H2	C/Q= -0.0237.C + 0.1802	- 42.1 ± 1	0.8064**	Log Q =0.8029+ 1.3024.log C	0.80 ± 0.002 C	2.23 ± 0.001 D	0.9974**
H3	C/Q = -0.0092.C + 0.1482	- 108.7 ± 0.68	0.6658**	Log Q =0.8541+ 1.181.log C	0.85 ± 0.01 B	2.39 ± 0.016 C	0.9973**
H4	C/Q= -0.0202.C + 0.1974	- 49.5 ± 1.76	0.8885**	Log Q =0.6813+ 1.4013.log C	0.68 ± 0.002 D	1.98 ± 0.004 E	0.9976**
LSD0.05					0.0165	0.0264	

The desorption Freundlich equations fitted well for P desorption isotherms for the various HA samples, and the correlation coefficients indicated that all of the relationships were statistically significant. It was concluded that the Freundlich equation is better than the Langmuir equation to describe desorption of P from the five soil samples with different H contents, except when high concentrations of Humic acid were added ($H \geq 1.6$ m.g^{-1}). However, Langmuir equation could not be use for calculating the relevant sorption parameters as was found by Wang *et al*., (2016).

3. Adsorption/Desorption:

The percent of desorbed-P relative to adsorbed-P (Dr %) was calculated. The Dr % value reflects the degree of desorption (Table. 4).

Unlike for the P adsorption characteristics, the Dr% values decreased as the HA content increased. Thus, a higher Dr% value indicating a stronger tendency for P to desorption, Like for Dm, the Dr % value was significantly higher for the HA_0 and HA_1 samples than for the samples with higher HA contents.

The mean of Dr % was 29.8 and 29.1 respectively, This indicated that P could be released into solution more easily from the ($HA \leq 1$ m.g^{-1}) sample (meaning it would be more bioavailable in the calcareous soil) than from the samples with higher HA contents.

Table. 4: Percent of P desorbed from the amount P adsorption (Dr %).

P-added (ppm)	HA_0	HA_1	HA_2	HA_3	HA_4
5	11.52	6.21	13.53	13.17	24.87
10	16.76	14.02	7.61	7.94	12.91
20	23.95	22.77	9.52	11.42	15.21
30	27.67	21.61	10.83	11.87	13.36
40	30.79	37.51	6.28	7.22	8.45
60	39.11	38.20	6.77	8.27	7.97
80	42.78	42.03	8.94	16.22	9.63
100	45.80	50.65	10.20	15.30	8.50
Medium %Dr	29.80	29.13	9.21	11.43	12.61
$LSD_{0.05}$	1.44	8.16	1.57	1.18	2.39

Different letters within a column are significantly different at P ≤ 0.05, (HA0=0, HA1=1, HA2=1.6, HA3=2.4, HA4= 4.8 mg HA/g soil).

This indicates that adding humic acid to calcareous soil increased P adsorption capacity, leads to decrease of bioavailable-P to plants. The Dr% rate was relatively increased when the P concentration in the solution was increased for (HA_0 and HA_1 treatments) to reach about 45.8% and 50.6%, respectively. Whereas, adding humic acid with the concentration HA_2 and HA_3 to the calcareous soils decreased Dr% by an average of 9.2% and 11.4% respectively.

Conclusion

The relationship between the HA content in calcareous soil and the adsorption and desorption of P was studied by parameter isotherms. The Langmuir and Freundlich equation fitted the adsorption isotherms for calcareous soil very well. Using Humic acid HA $\geq$1.6 mg.g^{-1}, the maximum adsorption of P is reached to 417 mg.kg^{-1} (HA_4 = 4.8 mg.g^{-1}). The use of humic acid decreased the desorption amount of P from the calcareous soil. However, if the HA concentrations are excessive, enough P fertilizer must be applied to maintain the supply of P to meet the needs of the crop for a long period of time.

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