Phosphorus isotherms sorption in semi arid soil

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Abstract - The aims of this study were to determine the phosphorus (P) adsorption capacity of the semi-arid soils from Tunisian Sahel and to generate that relates these capacities to soil properties. Air-dried samples soils collected at four depths from three sites in the Sahel region of Tunisia (Chott-Mariem, Enfidha and Kondar). Soil chemical, physical and mineralogical properties were analyzed. 0,5g of each soil samples were shaken with increasing concentrations of solution P for 36 hr at 20 °C. The maximum of P adsorption were greatly influenced by soil organic matter, calcium, magnesium and clay content. Moreover, the data obtained was fitted using Langmuir and Freundlich isotherm functions. P adsorption data revealed that Langmuir equation (R^2= 0.98) showed a better describe the adsorption phenomena over the Freundlich equation (R^2 =0. 96) in all the three series.

 Key Words: Phosphorus, adsorption isotherm, Sahel of Tunisia, Langmuir, Freundlich equations.

1. INTRODUCTION

   Phosphorus (P) is after nitrogen the second most important nutrient for plant growth and optimal yield production in cropping systems [1, 2]. Phosphorus also plays a central role for other living organisms such as microbes as it plays a predominant role in cellular metabolism such as ATP and as an important constituent of many structural and biochemical functional components [3]. During the last decades, the amount of economically-available reserves of rock phosphate decreased as a result of crop intensification to support the demand for food [4, 5]. Nevertheless, fertilizer P use efficiency in most cropping systems is still relatively low, less than 50% in field crops and around 20-30% in grasslands [6]. The biogeochemistry of P in soils is strongly influenced by the presence of minerals such as apatite, strengite, and variscite. The weathering of these soil minerals is generally too slow to meet crop demand for P. Furthermore, P bearing minerals including calcium (Ca), iron (Fe), and aluminum (Al) phosphates vary in their dissolution rates; depending on the size of the mineral particles and soil pH [7]. In neutral-to-calcareous soils, as those found in the sahel region of Tunisia, P applied as fertilizer is fixed onto the soil matrix through precipitation reactions [8] and adsorption on the surface of Ca-carbonate [9] and clay minerals [3]. The adsorption of phosphates is an approach wherein phosphate ions in soil solution react with cations on the surface of soils particles, and affects both the availability of P to plants and the fate of P fertilizer. In acidic soils, Zhang et al., [10] and Wen et al., [11] determined that P was dominantly adsorbed by Fe and Al oxides and hydroxides such as gibbsite, hematite and goethite. With increasing soil pH, Fe and Al phosphate solubility increases but solubility of Ca-phosphate decreases [1]. Phosphate can precipitate with Ca, generating di-calcium phosphate which is still available to plants. However, the di-calcium phosphate can be further transformed into more stable forms such as octo-calcium phosphate and hydroxyapatite, which are less available to plants at alkaline pH [12]. In neutral-to-calcareous soils, P retention is dominated

by precipitation reactions, although P can also be adsorbed on the surface of Ca-carbonate [9] and clay minerals [3]. The adsorption of phosphate is an approach wherein phosphate ions in soil solution react with elements on the surface of soils particles, and is an important property affecting both the availability of phosphate to plants and the fate of phosphate fertilizer. Other factors can limit P availability as well, such as the buffering capacity of the soil [13], the surface area [14, 15], nutrient balance, organic matter (OM) and crop husbandry practices [16]. In soil solution, dissolved phosphorus is composed of orthophosphate ($H_2PO_4^-$, HPO_4^- PO_4^{3-}) with different degrees of protonation depending on the pH. Orthophosphate strongly adsorbs through covalent bonding to soil functional groups forming stable bonds [17]. The soil matrix therefore acts as a sink that traps much of the orthophosphate found in the soil solution [18], with PO_4^{3-} having the strongest binding capacity to the soil functional groups at soil pH [19]. As a result, it was believed that P transport through subsurface runoff was negligible. Nevertheless, for the most highly fertilized soils added PO_4^{3-} may exceed the P sorption capacity of the soil, causing PO_4^{3-} concentrations to increase in the soil solution [20]. The adsorption is measured by shaking of the soil samples with standard phosphate solution, measuring the change in phosphate concentration and calculating the phosphate adsorbed. In solution, the concentration of phosphate is determined and the quantity of phosphate adsorbed is calculated. Freundlich and Langmuir adsorption isotherms models are mostly employed for understanding the relationship between the quantity of phosphorus adsorbed per unit soil weight and the concentration of phosphorus in solution and provide a distribution-equilibrium coefficient that describes the ratio of adsorbed to dissolved orthophosphates. They have previously been applied to a wide variety of soils [21], however none of which investigated P dynamics for the soils of Tunisia; in particular the soils of the Sahel region. This region is considered to be one of the most important areas for crop production in Tunisia. The aim of this study was to investigate the P adsorption capacity by three soil profiles from three different sites of the Sahel region and select from the two isotherms models the best fit for the data.

MATERIAL AND METHODS

Site description and soil characteristics

The P sorption experiment was conducted with soils from three sites of the Sahel region of Tunisia: Chott Mariem (35°54'N10°36'E), Enfidha (36°08'N10°22'E) and Kondar (35°55'N10°17' E). The climate is moderate in the winter and hot in the summer, with mean annual temperature of 23°C, and mean annual precipitation of 300 mm. The soil (0–25-cm) is fine sandy loam (*Isohumic* soils) at Chott Marien, clay soil (Calcic-magnesic) at Enfidha and Kondar (Solonetz) [22]. Chemical characteristics of the studied sites are presented in Table 1. The pH_{water} varied from 8.12 at Chott Mariem to 8.66 at Kondar, organic matter varied from 1.89% at Chott Mariem to 7,36 % at Kondar, Mehlich-3 P (P_{M3}) varied from 1.98 mg kg^{-1} at Kondar to 93.68 mg kg^{-1} at Chott Mariem, and Mehlich-3 Ca varied from 5450 mg kg^{-1} at Chott Mariem to 17784 mg kg^{-1} at Kondar. Triplicates soil samples were randomly collected at four depth, 0–25-, 25–60-, 60–90-, and 90–120-cm, air-dried, sieved (<2 mm) and stored until analysis. The soils were classified as *isohumic* soils for Chott Mariem, *calcic-magnesic* for Enfidha, and *solonetz* for Kondar. Soil pH was determined in a 1:2 soil: water suspension [23]; organic C (OC) by the wet oxidation method [24]; particle-size distribution by the pipette method [25] and calcium carbonate equivalent (CCE) by the $BaCl_2$ extraction method [26]. Mehlich-III [27] P, Ca, Mg, Fe, Al, Cd, Cu, Mn, were determined by equilibrating 2.5 g of air-dried soil with 25 mL of Mehlich-III extracting solution for 5 min and filtering through Whatman No. 40 filter paper. Concentrations of the various elements in the extracts were determined by inductively coupled plasma optical emission spectrophotometer (CP–OES, Perkins Elmer, Model 4300DV). The quantitative mineralogical analysis was extracted from the powder XRD data using an internal standard for each mineral [28]. The clay fraction was quantified, after purification, and based on a pure, standard clay mineral.

Batch experiment

Solutions with a range of P concentrations were formulated in a 0.01 mM CaCl matrix for batch equilibration with the air-dried soils. Initial equilibrating solution-P concentrations were selected to ensure that the upper concentration represent a distinct curvature of the plotted P sorption isotherm (0, 50, 100, 150, 200, 250, and 300 mg P L^{-1}). The sorption batch were replicated twice and consisted of mixing 0.5 g of air-dried soil with 25 ml of one of the equilibrating solutions. Each batch was shaken at 120 rpm on a horizontal mechanical shaker for a contact time of 36 h at 20 °C, and then filtered through Whatman no. 42 filter paper. The filtrates were colorimetrically analyzed for P at 882 nm using the ascorbic acid method [29], and the difference between amount of P in solution before and after equilibrium was assumed to equal the amount of P sorbed to the soil matrix. The experimental data were fitted using the Langmuir and Freundlich isotherms.

Data modeling

1-Langmuir adsorption-isotherm equation

$$Q = Q_{max} \times \frac{k_l \times C}{1 + k_l \times C} \quad (1)$$

Where Q (mg P kg^{-1}) is the adsorbed P onto the soil after 36-h contact, Q_{max} (mg P kg^{-1}) is the P sorption maximum; k_l (P mg.L^{-1}) is the binding energy of P, and C (mg P L^{-1}) is the equilibrium P concentration in solution (Barrow 1978).

2- Freundlich adsorption-isotherm equation

$$Q = k_F \times C^n \quad (2)$$

Where Q (mg P kg^{-1}) is the adsorbed P onto the soil after 36h contact, k_F is a coefficient, C (mg L^{-1}) is the equilibrium P concentration in solution, and n is a coefficient introducing non-linearity.

Statistical analysis

Non-linear regression techniques were applied to the sorption data using NLIN procedure (SAS Institute, 2001). Sorption was characterized by fitting Eqs. (1) and (2) to the plot of adsorbed P against equilibrium P concentration in solution. The fit of the regression curve was evaluated using the adjusted R^2 to determine how well the curve explains experimental data variation and the root mean square error (RMSE) which estimates the variation, expressed in the same units as the data, between theatrical and experimental values. This parameter is defined by the following formula:

$$RMSE = \left[\sum_{i=1}^{n} \left(\frac{Q_{the} - Q_{exp}}{n} \right)^2 \right]^{1/2}$$

Where: Q_{the} and Q_{exp} are simulated and observed values, respectively. The RMSE tests the accuracy of the model, which is defined as the extent to which simulated values approach a corresponding set of measured values [30].

RESULTS AND DISCUSSION

Soil Characteristics

The pH, particle size distribution, and concentration of major elements within the different soils are indicated in Table 1.

All of the different samples were alkaline for all depths with the pH generally above 8. The texture for the Chott Mariem site varied with depth, and ranged from a fine sandy loam to clay. Soil texture Kondar for the varied to clay a heavy clay. Finally, in the profile texture soil site of Enfidha, only heavy clay texture soil was determined at different horizons. The variation in texture reflects the differences in parent materials [31]. Clay content in particular can affect soil behaviour, fertility, water and nutrient holding capacities as well as plant root movement [3]. The Enfidha soils with their high clay content would probably hold more water and nutrients than the two other soils. It would also likely have a high phosphorus fixing capacity [32].

Soil OM content reflects the level of soil fertility [33] and was highly variable between the various sites and horizons (Table 1). For Enfidha soils, the OM content was similar for all depths, with a mean of 3.16%, which was relatively high compared to the other soils. This is likely due to migration of OM to deeper horizons and it's incorporation with the particle size of clay under the action of microbial activity [34]. In the Chott-Mariem soils, the majority of OM accumulated at depth, primarily between 60 and120 cm. By contrast, the soil profile from the Kondar site contained very high rates of OM in the surface horizons (i.e. 0-25 cm and 25-60 cm), which decreased with the depth. In general the

distribution of level of organic matter is influenced by different factors such the amount of organic matter and the soil texture, especially clay content [35,36]. The mineral content (phosphorus, calcium, magnesium, potassium, iron and aluminum) also differed markedly between the soils. The Ca content was particularly different and varied between less than 6 mgkg^{-1} dry weight in the

surface horizon for the Chott-Mariem profile to more than 20 mgkg^{-1} dry weight for the deeper horizon from the Kondar profile. The values for the soils were high and in all instances increased with depth. By contrast, available P, in the two of the three soils was low and in all profiles soil P decreased with depth.

Table1. Samples Soils characteristics

	Chott-Mariem site				Enfidha site				Kondar site			
Dept(cm)	0-25	25-60	60-90	90-120	0-25	25-60	60-90	90-120	0-25	25-60	60-90	90-120
pH (H$_2$O)	8.12	8.41	8.56	8.54	8.26	8.14	7.97	7.87	8.66	8.86	8.35	8.12
OM (%)	1,89	1,42	3,61	4,66	3,48	3,18	3,19	3,08	7,36	7,13	5,68	1,89
P(mg/kg)	93,68	20,90	4,12	4,99	4,48	2,19	3,70	3,79	1,98	1,53	1,27	1,91
Ca(mg/kg)	5450	5508	5874	5450	10026	9495	7885	11360	17784	10108	12786	20337
Al(mg/kg)	76	87	72	51	230	159	108	198	34	19	14	34
K (mg/kg)	491	299	135	106	294	310	298	376	143	129	160	234
Fe(mg/kg)	33	24	9	3	41	41	45	44	12	19	30	31
Mn(mg/kg)	410	433	356	461	668	774	717	841	680	963	1000	966
Clay	12.8	24.4	30.5	25.8	63.3	76.1	78.8	77.5	58.6	56.8	51.5	71.8
sand	49.2	60.4	59.5	59.1	20.7	13.9	12.2	10.5	28.6	26.8	46	24.2
Silt	38	15.2	10	15.1	16	10	9	12	12.8	16.4	2.5	4
Texture	Fine sandy loam	Loam sandy clay	clay	Loam sandy clay	Clay	Heavy clay	Heavy clay	Heavy clay	Clay	Clay	Sandy clay	Heavy clay

Phosphorus adsorption capacity

The results of the physico-chemical and mineralogical illustrated in the Tables 1 and 2 show that there is some correlation between the amounts of P adsorbed and the different compositions in all the soils. In fact, the amount of P adsorption have a positive correlation with the clay content, organic matter and calcium exchangeable, with organic matter (OM) and magnesium exchangeable and with organic matter, exchangeable magnesium and iron cations respectively in the profile soil of Chott Mariem, Enfidha and Kondar. This correlation was also observed by Akhter et al., [37]. The positive relationship of P adsorption with clay content may be related with larger surface area of clay as compared to sand [38]. It could also be related to the relatively large number of positive charges that can react and strongly bind the negatively charged phosphate ions in soil solution. Barbieri et al., [39] and Broggi et al., [40] indicated that the adsorption

of P on the clay fraction is assigned to the variable electrical loads of the edges of the sheets of the clays, especially present in the kaolinite and smectite. However, our X-ray analyzes have revealed an abundance of kaolinite and smectite in our soils (Table 2).

Positive relationships of organic matter and P adsorption had also been reported by several researchers. Jelali et al. [8] showed that coefficient for soil OM to predict maximum P adsorption had positive sign and the soils with high OM had poorly crystalline iron oxides suggesting inhibiting effect on iron oxide crystallization through complexation increasing sorption capacity for phosphate. Additionally [41] found that the role of organic matter in increasing the ability of soils to adsorb P that is attributed to its association with cations such as Fe, Al and Ca. On the contrary, negative relationships between the organic matter contents of soils and P adsorption was reported Waheed et al

[42]. They found that the presence of organic matter on highly weathered soils reduces P

adsorption capacity. This reduction may be due to direct result of competition for adsorption sites

Table 2: Mineralogical composition of the different soils profiles

Profiles	Depths	Identification of mineralogy					
		Kaolinite	Quartz	Calcite	Smectite	Illite	chlorite
Chott-Mariem	0-25cm	+	+++	+	-	-	-
	25-60cm	-	+++	+	+	-	-
	60-90cm	+	+++	+	+	+	-
	90-120cm	+	+++	++	+	+	+
Enfidha	0-25cm	+	+++	++	+	-	+
	25-60cm	+	+++	++	+	+	-
	60-90cm	+	+++	++	+	+	-
	90-120cm	+	+++	++	+	+	+
Kondar	0-25cm	-	+++	+++	+	-	-
	25-60cm	+	+++	+++	+	-	+
	60-90cm	+	+++	+++	+	+	+
	90-120cm	+	++	++	+	+	+

+++ Abundant, ++ moderately abundant, + poorly abundant

between phosphate and organic ligands. There was also suggestion of possible reduction of organic matter enhance the positive surface charge by lowering pH. This decreases the attraction of P to the soil surface. The relationship between exchangeable calcium and the soil adsorption capacity showed that as the exchangeable calcium increased, the adsorption capacity also increased [43]. Similar observation has been reported for

Iranian soils [8]. It has been suggested that increases in P adsorption at high pH values have frequently been ascribed to the precipitation of calcium phosphorus. This phenomenon is related to the high levels of calcium existed, such in our case. The Ca-minerals promotes the formation of highly reactive polyhydroxides, and enhance the adsorption of phosphorus on calcium compound [44].

Adsorption modeling

The relationship of soluble and adsorbed P was best described using the linear form of the two equations of Langmuir and Freundlich models, Figs (1. 2 and 3). The data thus obtained are presented in Tables 3. Application of the Langmuir equation indicates that the sorption phenomenon was adequately described by this isotherm. It can be provided a strong fit adjusted R^2 (R^2 =0.98) and weakness values of RMSE for all layers of different profiles except in the layer of (60-90cm) of Chott Mariem profile witch it recorded a low value of R^2 = 0.93 and a high value RMSE= 0,136.The values of maximum adsorption capacity (Q_{max}) determined using Langmuir model was higher than the experimental adsorbed amount and corresponded to the adsorption isotherm plateau, which is unacceptable. The value of k_L (Lmg^{-1}) parameter of

the Langmuir model is the constant representing the affinity of sorbate to sorbent. Higher b values mean more affinity of sorbate to sorbent. Comparison of these values with k_L parameter of the Langmuir model in this study reveals that the sorption affinity of P to samples soil Chott Mariem is lower than the affinity of Enfidha and Kondar. Both the Q_{max} and binding energy (k_L) values indicated that P adsorption capacity as suggested by the population of sites in the low equilibrium P. High k_L values observed in this experiment show that the tenacity of phosphorus sorption is greater at low P equilibrium concentrations. Q_{max} tends to be correlated with soil organic content (Zhong et al., 2012; Rogan et al., 2010) because the OM controls P sorption capacity [45, 46]. Processes for the control of sorption maxima and the affinity

constants by organic amendments include the competition of organic acids produced during mineralization for the same sites of phosphorus fixation and the complexing of exchangeable Al by organic acids [47, 48]. Furthermore, both sewage sludges contain inorganic ligands such as SO_4^{2-} which can complex exchangeable Ca and Mg which may form soluble complexes with P in the soil solution [49].

As shown in Table 3 the Freundlich model also could not describe the sorption of P onto soil samples acceptably, because this model also assumes a different behavior for the sorption of a P onto soil samples and its corresponding R^2 and RMSE values in Table3 concurred with this result. The exponent (n) found in all equations was greater than 0.47. The Q_e data revealed that maximum P adsorption ($8.995mg.g^{-1}$) occurred in the deepest Kondar horizon (90-120cm) while the minimum value was observed in the surface horizon (0-25cm)

of Chott Mariem site profiles with a value of $3,083mg.g^{-1}$. Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the sorbent by the sorbate. Whereas the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the samples soil surface; since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous. Comparing the two equations it may be concluded the Langmuir model showed a better fit to the data than the Freundlich model. By cons some others works have been reported that the Freundlich model model was a better fit than Langmuir model including Dubus and Becquer, [50,51,52].

Table3. Phosphorus characteristics of soils profiles using the Langmuir and Freundlich equations at three sites in the Sahel region of Tunisia.

	Depths (cm)	Langmuir					Freundlich			
		Q_{max} (mg.g^{-1})	R^2	Q_{the} (mg.g^{-1})	K_L (min^{-1})	RMSE	R^2	Q_{the} (mg.g^{-1})	1/n	RMSE
Kondar	0-25cm	13.61	0,99	23.16	0,267	0,465	0,99	4.97	0,608	0,574
	25-60cm	14.22	0,99	20.79	0,381	0,357	0,99	5.74	0,541	0,612
	60-90cm	14.6	0,99	27.39	0,346	0,598	0,99	6.95	0,64	0,583
	90-120cm	14.86	0,99	21.68	0,794	0,645	0,97	8.95	0,538	0,939
Enfidha	0-25cm	14.75	0,98	24.33	0,304	0,713	0,99	5.86	0,593	0,479
	25-60cm	14.67	0,98	27.87	0,163	0,619	0,99	4.34	0,649	0,504
	60-90cm	14.66	0,99	21.78	0,322	0,635	0,96	5.29	0,574	0,111
	90-120cm	13.95	0,98	19.49	0,473	0,769	0,96	5.98	0,544	0,975
Chott mariem	0-25cm	14.86	0,95	19.06	0,11	0,106	0,89	3.08	0,474	0,168
	25-60cm	14.7	0,99	21.28	0,129	0,53	0,97	3.18	0,56	0,84
	60-90cm	14.83	0,93	24.27	0,296	0,136	0,88	5.63	0,587	0,18
	90-120cm	14.96	0,99	19.49	0,688	0,407	0,95	7.35	0,484	0,124

Q_{max} = P sorption maximum; b= binding energy of P, Q_{the} = P theoretical sorption; n is a coefficient introducing non-linearity,

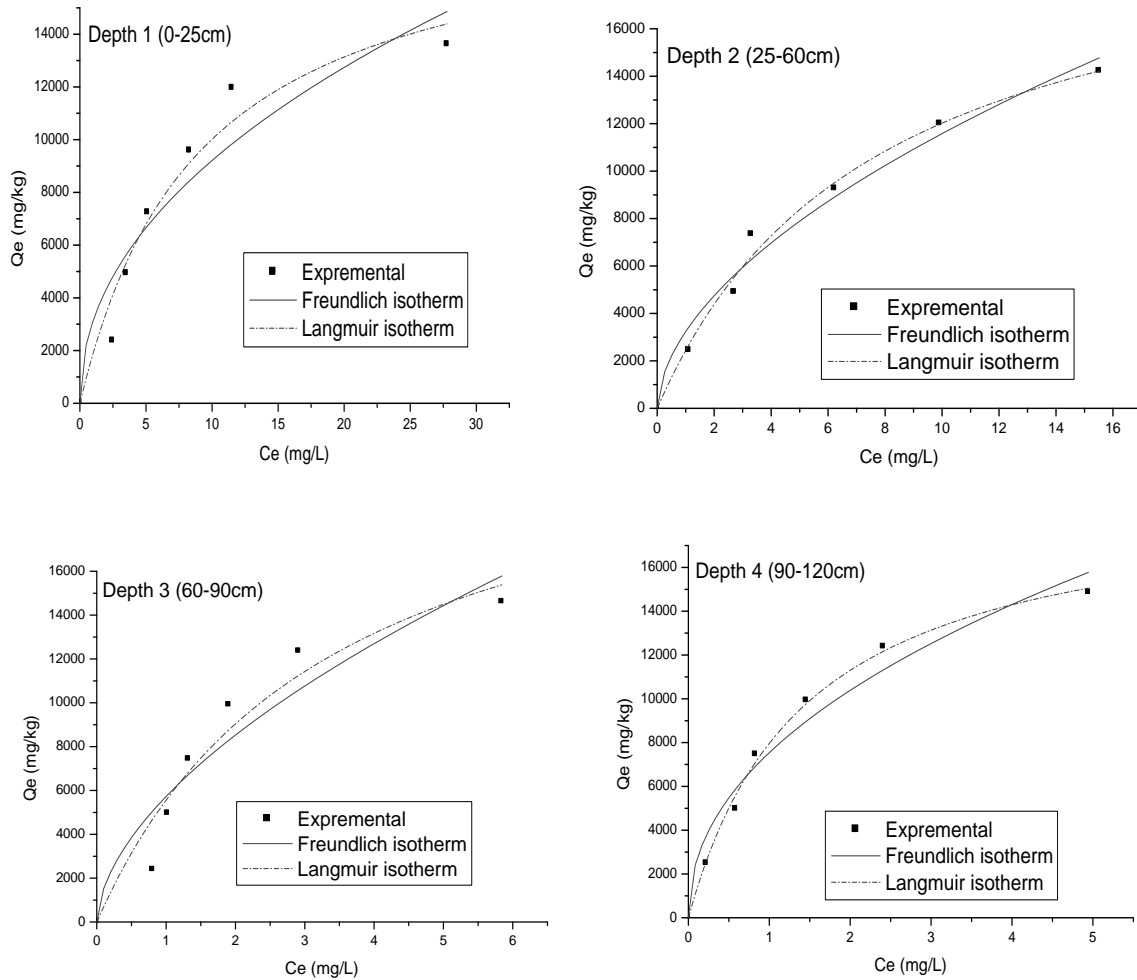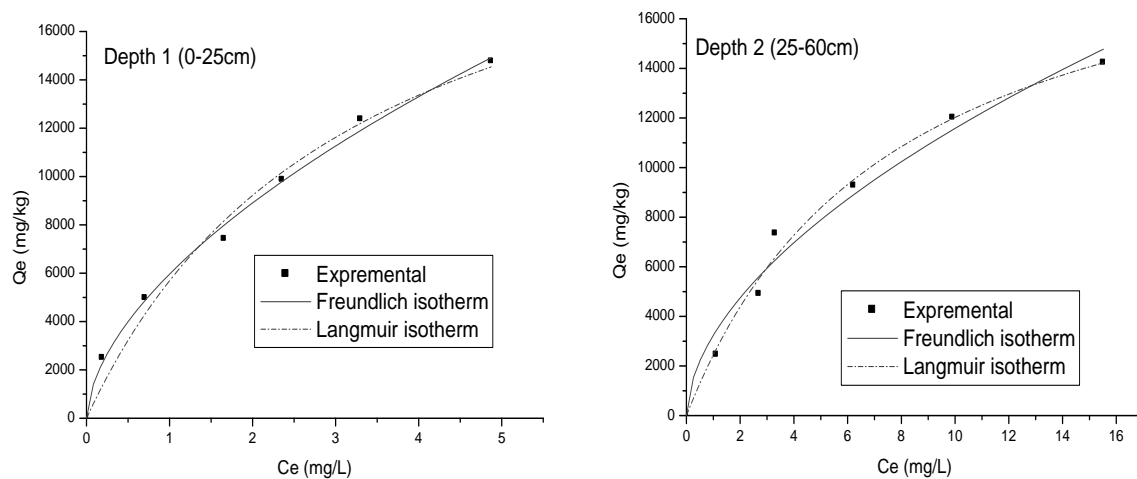RMSE = root mean square error probability.

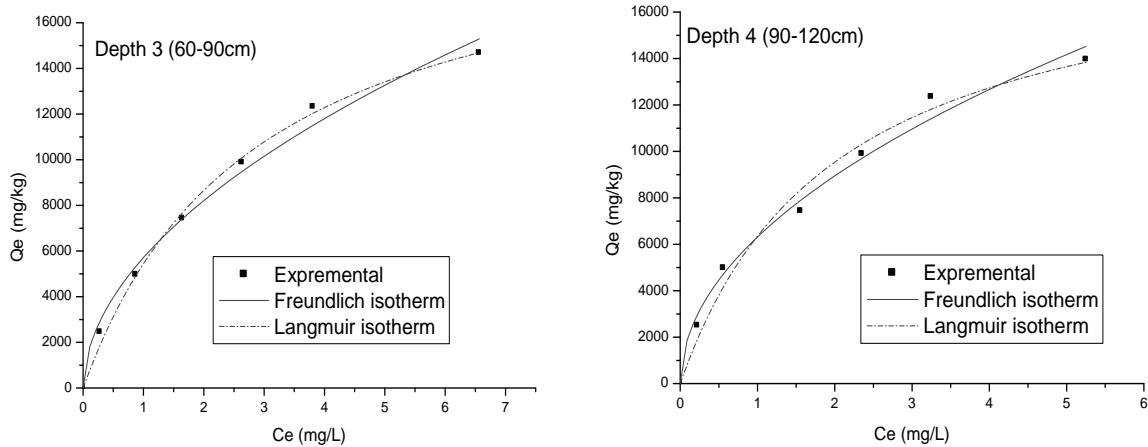Fig. 1: Phosphorus (P) sorption Langmuir and Freundlich isotherms of the all profiles soils of Chott Mariem

Fig. 2: Phosphorus (P) sorption Langmuir and Freundlich isotherms of the all profiles soils of Enfidha
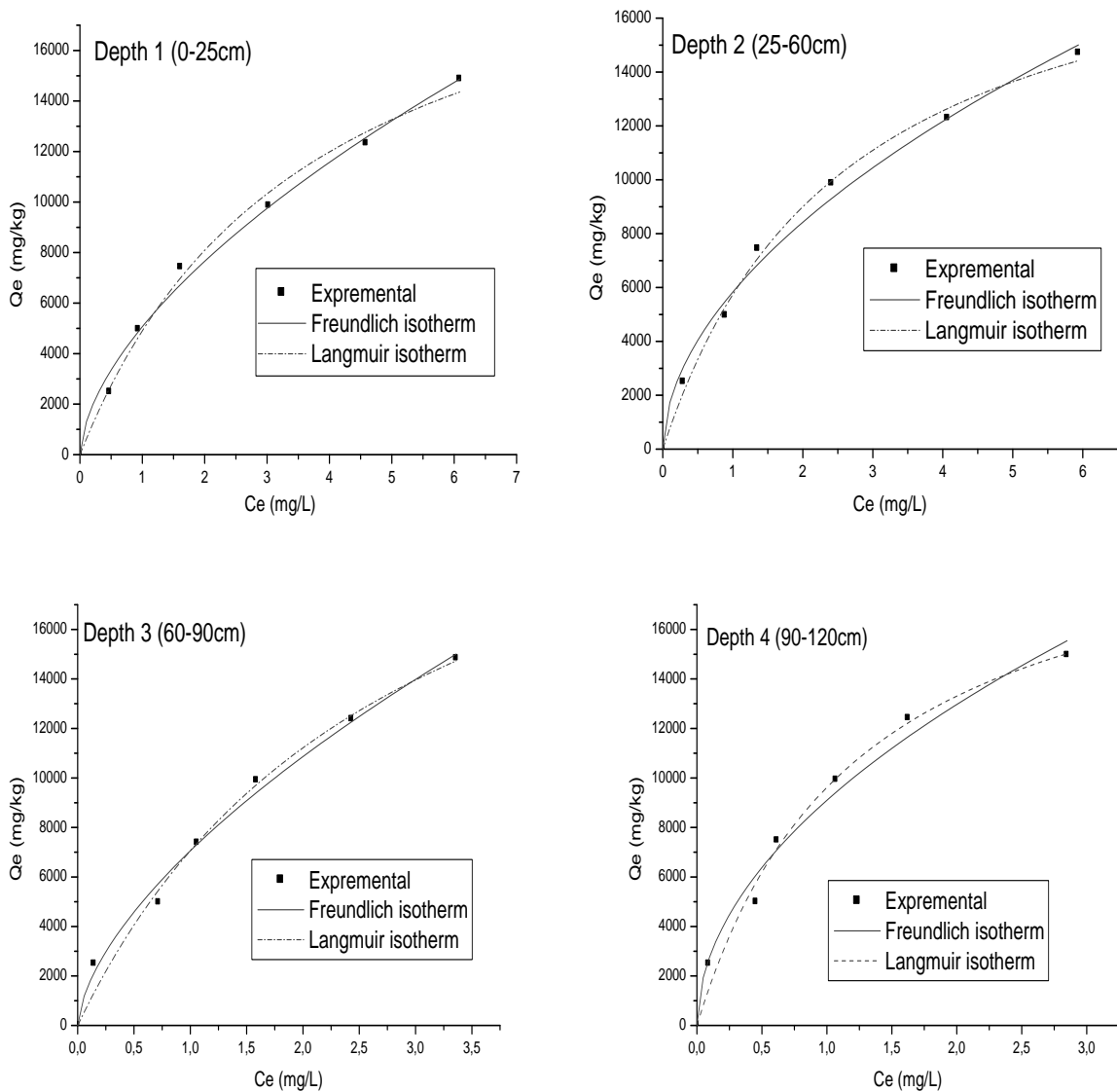

Fig. 3: Phosphorus (P) sorption Langmuir and Freundlich isotherms of the all profiles soils of Kondar

Conclusion

The results of this study indicate that the different profiles of various sites alkaline soils for the Sahel region have high phosphate adsorption capacities. The adsorption isotherm showed different curves for the three soils. From our data, it can be seen that the soils samples with high organic matter, exchangeable Ca, exchangeable Mg and clay content sorbed significantly more P. Phosphorus adsorbed may be more or less available depending on the strength of the interaction and type of compound formed. It is known that minerals such as hydroxiapatite can be very stable, decreasing plant available phosphorus [53]. By contrast, soil samples rich in organic matter (e.g. surface horizons of Kondar site) had lower phosphorus adsorption. This suggests that use of organic matter can be a useful management practice for controlling P sorption and hence increase fertilizer use efficiency in these soils. Langmuir and Freundlich equations were used to describe P adsorption processes. The results indicate a better fit with the Langmuir model.

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