

# Study the Behavior of Phosphorus Added to Soil in Wadi Etba, South-West Libya

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## Abstract

The aim of this study was to investigate the adsorption of phosphorous to soils and its availability to be active in Wadi-Etba region (south west of Libya). The effects of some properties of these soils on phosphorous adsorption have been studied and characteristics of adsorption have also been investigated. Seven soil samples were collected from private farms. The chemical and electrochemical analysis data were used to evaluate the adsorption parameters for study of different phosphorous adsorption isotherms in these soils. The adsorption process was tested by applying Freundlich, Langmuir Model isotherms. The isotherms parameters ( $K_f, n$ ), ( $b, K_L$ ), ( $K, y$ ) were used to predict the type of adsorption layer, the active Sites involved in adsorption process and adsorption capacity of phosphorous onto soil. The results showed low adsorption of phosphorus onto all studied soils and quantity of adsorbed phosphorous different with different additional initial concentration and studied soil properties. The adsorption isotherms for phosphorous adsorbed onto all studied soils were of S Shaped according to Giles classification and followed the fitting data of Freundlich equation. This was discussed on the basis that Unequal energy of adsorption centers developed that may allow to adsorption multilayers on soil surface, The results showed different adsorption capacity for studied soils and found to be decreased as: Tokrotan < Om Alhman < Tasawa < Dojal < Sobaitat < Marhba < Agar. The negative values of free energy ( $\Delta G$ ) showed that the adsorption process of phosphorous was spontaneous Thermodynamically and related significantly to freundlich ( $K_d$ ) constant.

## Keywords

Adsorption, Phosphorous, Soil, Wadi-Etba, Freundlich, Langmuir Isotherms

Received: June 16, 2021 / Accepted: August 3, 2021 / Published online: August 20, 2021

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## 1. Introduction

It is known that many types of soil lose several of their nutrients either as a result of the displacement of cultivated crops or as a result of washing and drifting processes, and the process of loss is often faster than the process of compensation for the decomposition of mineral rocks and organic matter in the soil, thereby disrupting the balance, a

breach that causes the need for mineral and organic fertilization.

Phosphorus is similar to nitrogen and potassium in how important it is to the plant despite its presence in the tissues of the plant in minor quantities, where the plant absorbs this element in order to meet its needs for various vital processes such as photosynthesis, intention formation, cell division, seed formation, cellular process organization and genetic trait

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transfer. Phosphorus also plays a key role in the generation of energy.

Soil varies in terms of its total phosphorus content influenced by many factors, the most important of which is the substance of origin, agricultural exploitation, climate and others. In general, the soil content of total phosphorus is in the range of (0.02-0.15%) and is associated with the presence of organic matter, where organic phosphorus accounts for 20-80% of total phosphorus [1]. Total phosphorus in the soil does not have to be a good measure of the amount of the prepared phosphorus for plant growth, because a large part of phosphorus may exist in a way that is difficult to take advantage of, as the plant obtains phosphorus from the soil solution mainly in the form of di-hydrogen ortho-phosphate ions ( $\text{H}_2\text{PO}_4^{-2}$ ). While the largest proportion is prone to sedimentation and stabilization reactions (adsorption) where phosphorus changes from prepared to unprepared form, leading to the complete non-utilization of phosphorus due to its loss [2]. Based on information from soil analysis laboratories in the United States, the world's highly soiled phosphorus content ranges from very low to medium, and phosphorus is the most deficient after nitrogen for plant growth in the earth.[3]

Most of the phosphate fertilizers added to the soil are initially semi-stable calcium phosphate compounds and the plant can benefit from them until over time, they become less soluble and more stable forms, where it is difficult for the plant to benefit. When phosphate fertilizers are added to the soil, some phosphates will be installed and the other part will be deposited in a form that is not prepared for plant growth due of the interaction between fertilizers and soils. [4]

There are many factors that affect the viability of phosphorus and these factors are common to almost all types of soil, including the amount of clay in the soil, where by increasing the installed amount of phosphorus, the amount of phosphorus increases due to the increase in the specific surface of clay granules. The duration of the reaction between phosphorus ions and soil components also increases with the stabilization rate, and the time varies from soil to another, and the longer the plant is able to make the most of the added phosphate fertilizer is practically important. In soils with a high stabilization capacity, this period is small, while in other soils the period may be longer for a month or more, depending on whether the fertilizer is added in one batch or in batches during the agricultural cycle. Also the pH of the soil, which is considered to be a high-impact factor in determining the viability of the phosphorus for the plant, It has also been mentioned that the ionic form of phosphates preferred for plant absorption is  $\text{H}_2\text{PO}_4^{-2}$  compared to other ionic images. The concentration of these forms decreases by the change of the pH depending on the method of stabilization, and the highest phosphate validity in the PH range of 6-7.

The Organic matter is also one of the factors on the availability of phosphorus to the plant, where it is known that organic fertilizers when added to the soil increase the fertility of these soils, whether as a result of their elements or indirectly by increasing the melting of certain elements and making them in a soft form for the plant, including phosphorus. Temperature is also a factor where it is known that the rate of chemical reactions increases by increasing the temperature and therefore it has been found that the stabilization of phosphorus in the hot zone is greater than in mild regions, and the stabilization in the tropics is caused by the hexagonal oxides to increase the content of these soils from these compounds.

The physiological effect of chemical fertilizers where the Ammonic fertilizer has an acidic effect and thus reduces soil's pH which helps to melt phosphates. Therefore, studying the basis of stabilizing and limiting phosphorus with changing soil characteristics will help to understand and increase knowledge of raising the efficiency of phosphate fertilization, which has economic indicators and implications from an agricultural and environmental point of view. Normally, at the high level of phosphorus extracted, there is no response to the addition of phosphorus, the response is moderate at the intermediate level, while the response is high in the case of the low levels of phosphorus extracted.

The aim of this study is to track phosphorus adsorption in the soil of the study region and to determine its readiness in an effective form and to study the extent to which certain properties of this soil affect phosphorus adsorption as an essential element in soil productivity using the analytical data and the application of the adsorption isotherms.

## 2. Experimental

### 2.1. Study Area

#### 2.1.1. Geographical Location

The study area is located in the south-west of Libya in the southern part of Murzuq basin in the Fazan region, bordered to the east by Ben Ashhab mountain and Abad mountain, to the west of the Zarqan forest, to the west by the international border between Algeria and Niger and extends to the north-east from Bir Ain al-Zan, then by the Amsak Mountains, and even to the Mountains of Hamada Murzuq at the Fao, and from the south the border in the middle of the distance with the Qtaron region. And from the north are the mountains separating the Wadi-Etba valley and Wadi-Alhaa valley the form of a continuous strip from Sabha to the east to Erawan to the west. The valley consists of eight regions, respectively arranged from west to east, Maknoussa, Tasawa, Agar, Tokroten, Om Alhmam, Marhba, Dojal, Sobaitat, as in Figures 1 and 2 With population about 23,000.



Figure 1. Map of Libya shown (Wadi-Etba) study area.

The soil of the region, which covers most of the south and center of the country, is a desert sandy soil formed by harsh natural conditions and takes various forms, such as dunes, to areas covered by gravel and stones to semi-barred grass hills (Hamada) and to fragile, un-coherent and wind-affected soils. [5]

### 2.1.2. Vegetation

The region is considered to be a poor area with natural vegetation due to the harsh climatic conditions that are not suitable for its growth, so some desert plants that avoid drought or adapt, due to the lack of rain, high temperature, high evaporation and low humidity, grow in the region. Plants can adapt to their dry environment in several ways, including short-lived ones, some of which extend their bodies to the ground to reach near-surface water such as Tamarix, Cactaceae, etc., or by creating a waxy layer on their leaves such as Juncus acutus and Alhagi. [6]

## 2.2. Methods

### 2.2.1. Sampling

samples were collected from different locations in the study area where samples were taken from farms located in (Tasawa, Agar, Tokrotan, Om Alhmam, Marhba, Dojal, Sobaitat) the depth of sampling (5 cm), samples were kept in the laboratory for drying and disposal of gravel and excess materials not belonging to the soil by sifting them with a 2 mm sieve.

### 2.2.2. Measurement and Analysis

Electrical Conductivity (EC): for soil-to-water (1:1) extracts, using the Laboratory meter Conductivity) calculated at 25°C, by applying the Equation No.60 in 1954 Hand Book. [7]

PH: The pH of soil extracts was measured by using (Beckman digital PH meter).

Organic Matter Estimate: The proportion of organic matter was measured using the walkely and black method. [8]

Calcium carbonate Estimation: Richards method was used to estimate the Calcium carbonate content in the soil by reactive to hydrochloric acid and to calibrate acid that did not react with sodium hydroxide. [9]

Ready Phosphorus Estimation: a Murphy, Riley method has been used to estimate phosphorus. [10]

Time of Contact Determination: For the purpose of determining the equilibrium time between the adsorbent material and the adsorbent surface,  $\text{KH}_2\text{PO}_4$  phosphate solution was prepared at a concentration (50 mg/L), then (5 g) of soil were taken and placed in a conical flask, and (100 ml) of di-hydrogen potassium phosphate solution ( $\text{KH}_2\text{PO}_4$ ) was added, and electrically rejuiced. The absorption was then measured by the spectrophotometer for the first flask after 15 minutes, the second flask after 30 minutes, the third flask after 45 minutes, and the fourth flask after 60 minutes. The same steps were taken for each soil under study and it was noted that the equilibrium time was 60 minutes.

Adsorption curves: Standard solutions of  $\text{KH}_2\text{PO}_4$  were prepared in standard 250ml flasks with stocks (2.5, 5, 10, 20, 40, 60.80) mg/L and then took (5g) of soil and placed in conical flask, added to Each 100 ml of ( $\text{KH}_2\text{PO}_4$ ) solution and suspended and left for a balance period of 60 minutes, the concentration of phosphorus was estimated according to the Riley, Murphy method [10], and the amount of phosphorus absorbed was calculated from the following equation:-

$$Q_e = (C^\circ - C_e) \cdot V \text{ soil} / M \quad (1)$$

where: -  $Q_e$ : Amount of absorbed material (adsorbed phosphorus) (mg/g)

$C^\circ$ : Initial concentration of the material (added phosphorus concentration) (mg/L)

$C_e$ : concentration at equilibrium of the absorbed material (mg/L)

V: Total volume of the absorbed material solution in liters.

M: weight of soil per gram

Application of adsorption Models: The adsorption charts are specialized in describing how the materials intended for adsorption are interlinked, and two models have been selected to apply to the results obtained in practice, Freundlich and Langmuir Models, where the analysis of the results of these models gives a better perception of the description of the adsorption process. [11]

Application of Freundlich Isotherm model: This model assumes that the adsorption sites are unequal in their energy, allowing multi-layered adsorption to occur, and the linear equation of this model is the following equation:

$$\log q_e = \log k_d + 1/n \log C_e \quad (2)$$

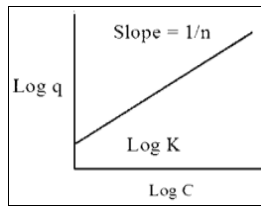


Figure 2. Freundlich Isotherm model.

Kd: constant of adsorption capacity  
 n: constant of adsorption intensity

Application of the Langmuir isotherm model: the second model used to study and interpret the adsorption process is the Langmuir model, which assumes that there are many link sites that are homogeneously distributed on the adsorbed surface, and these sites have the same adsorption viability, resulting in the formation of a single layer of the adsorbed material molecules, at the same time, assumes the absence of interaction between the adsorbed molecules. the linear form of the Langmuir equation is:

$$C_e \backslash q_e = 1 \backslash b \times q_{max} + C_e \backslash q_{max} \tag{3}$$

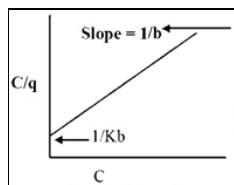


Figure 3. Langmuir isotherm model.

Where: b: constant of adsorption energy  
 q<sub>max</sub>: constant of the maximum amount of absorbed material.

Table 1. Averages of General Characteristic Values of Study area Soil Extracts.

	pH	EC (ml/cm)	Calcium carbonate%	Organic Matter%	Ready Phosphorus (mg/L)
Sobaitat	5.9	1.22	18.75	1.99	0.086
Dojal	6.5	0.07	16.25	2.16	0.046
Tokroten	6.9	0.53	11	3.06	0.022
Marhba	7.7	0.66	19	2.76	0
Om Alhmam	7.6	0.04	19	0.92	0
Agar	6.9	1.01	17.5	4.22	0.121
Tasawa	7.4	0.35	15.5	1.15	0

### 3.2. The pH Values

The results shown in Table 1 and Figure 3 indicate that the pH rate for these samples ranges from the base and neutral medium (5.9-7.7) which are close to the neutral medium, in line with (FAO, 2005) [13], as the pH of the dry area soils is usually neutral to basic. The difference in pH values for soil is due to the difference in the soil content of ions that play an important role in raising or reducing their value. [14]

### 3.3. Electrical Conductivity (EC)

Salinity is estimated on the basis of electrical current conductivity [15], and the results in the study area shown in figure 4 showed the difference in electrical conductivity

Estimate free energy of adsorption: by means of free energy values, we determine whether the reaction is spontaneous or non-spontaneous [12], where estimated by the following equations: -

$$K = 155.5 \text{ Exp}(-\Delta G^\circ / RT) \tag{4}$$

$$\Delta G^\circ = -RT \ln K \tag{5}$$

Where: R=8.32 Jol/mol × kelvin T=303 Kelvin

Represents free energy and is estimated by the following equation: -

$$\Delta G^\circ = -2520.96 \times \ln (k/0.018)$$

$$\Delta G^\circ = -2520.96 \times 2.303 \log(k/0.018)$$

## 3. Results and discussion

### 3.1. Effect of Some Soil Properties of the Study Area on Phosphorus Adsorption

The results indicate that the amount of adsorbed phosphorus varied according to the difference between the initial concentration added and the properties of studied soil, where the variation in the soil properties had a clear effect on the difference in the amount of phosphorus adsorbed on the surface and the remaining phosphorus in the equilibrium solution.

values in most soils where the EC values of the soil studied were (0.04 - 1.22 m/cm) at 25°C. Agar and Sobaitat soils showed a higher values of the electrical conductivity, while Om Alhmam and Tokroten showed a marked decrease.

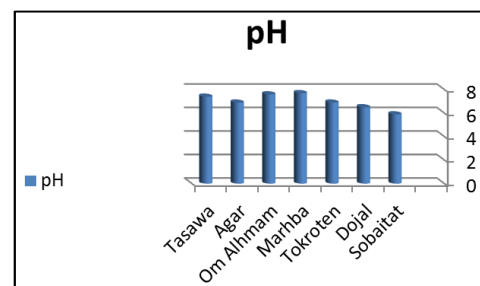


Figure 4. pH concentration of soils in the study area.

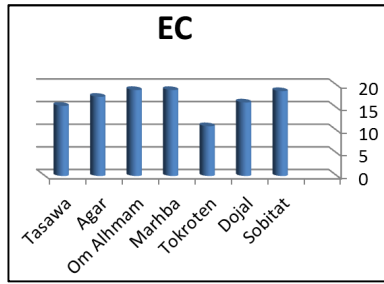


Figure 5. Electrical Conductivity values of soils in the study area.

### 3.4. Organic Matter

The results shown in Figure 5 indicate that the percentage of organic matter in these samples ranges from (0.92-3.06%), showing a decrease in the soil content of organic matter, as point out by (1985 henry foot) [16], which stated that the soil content of dry areas of organic matter is generally low and may not exceed 1% and may reach 3%.

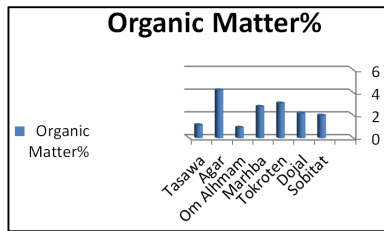


Figure 6. Percentage of Organic Matter of Soils in the Study area.

### 3.5. Calcium Carbonate

Through the results referred to in Table 1 and Figure 6 of the studied soil samples, it is clear that the percentage of calcium carbonate ranges from (11-20%). The highest percentage was in the Agar region (22%). The effect of calcium carbonate has been observed by increasing the percentage of ready phosphorus, which decreases with the increase of CaCO<sub>3</sub>, and this is consistent with (Awad 1984, Al-Shater1996) where it explained that the increase in calcium carbonate leads to a decrease in the availability of the original and added phosphorus in the form of phosphate fertilizers. [17, 18]

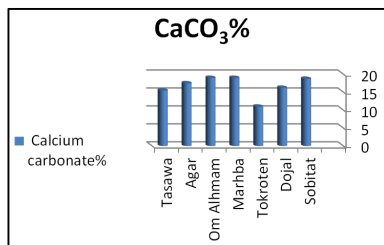


Figure 7. Percentage of calcium carbonate in Soils in the Study area.

### 3.6. Ready Phosphorus Before Addition

The results shown in Table 1 and Figure 7 for the regions under study indicate that the values of ready phosphorus in the

studied soil samples ranged from (0.021-0.116) mg/L. The lowest value was found in Tokroten area (0.21) mg/L, and the highest value was found in the area of agar (mg/L) (0.121).

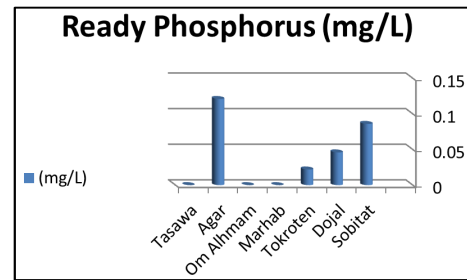


Figure 8. The ready phosphorus in soils of the study area.

### 3.7. Ready and Adsorbed Phosphorus After Addition

#### 3.7.1. Concentration of Ready Phosphorus

The results obtained and described in Figure 8, show that the concentration values of Ce in the soil samples added to different concentrations of added phosphorus (C<sub>0</sub>) varied according to the characteristics of that soil, at the concentration of added phosphorus (2.5, 5, 10, 20, 40 mg/L) was the highest concentration of Ce phosphorus in the equilibrium solution of the soil extract of Om Alhmam which was (0.172, 0.252, 0.355, 0.592, 0.658) mg/L respectively, and at the Added phosphorus concentration (60, 80mg/L) was the highest concentration of ready phosphorus after equilibrium in the soil extract of Tokroten (0.957, 1) mg/L respectively, on the other hand, the lowest concentration of ready phosphorus was at the concentrations of added phosphorus (2.5, 10.5) mg/L was in Dojal soil extract (0.052, 0.121, 0.086(mg/L) respectively, while at concentrations C<sub>0</sub> (60, 80) mg/L the concentration of ready phosphorus in the equilibrium solution in Tasawa soil extract was 0.527 0.593 (mg/L) respectively.

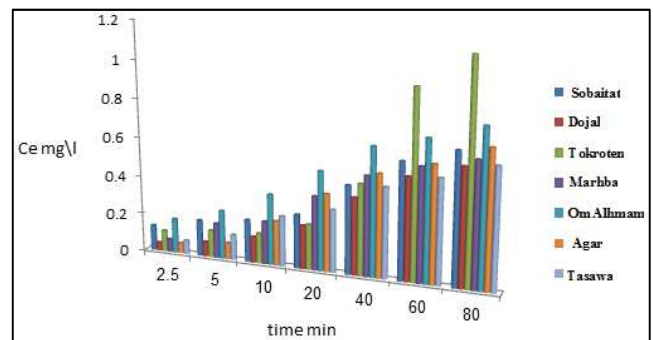


Figure 9. Ready phosphorus values in studied soils.

#### 3.7.2. Values of Adsorbed Phosphorus After Equilibrium

The lowest values of adsorption at concentrations of added phosphorus ( 2.5, 5, 10, 20 mg/L) were in Om Alhmam soil (0.046, 0.095, 0.193, 0.388 mg/g) respectively, and at the added

phosphorus concentrations (0.095, 0.193, 0.388 mg/g) respectively, and at (60, 80 mg/L) were the lowest in Tokroten soil (1.180, 1.582 mg/g) respectively. Thereby Om Alhmam and Tokroten soil had the lowest adsorption values at different concentrations of added phosphorus comparing to the rest of soils samples. due to their organic content and their important role in increasing the solubility of phosphate compounds.

### 3.8. Determining the Adsorption Curve

The relationship between the amount of adsorbed phosphorus ( $q_e$ ) and the concentration of ready phosphorus at the equilibrium ( $C_e$ ) was drawn to give the overall shape of the adsorption model, and it turns out that the general shape of the phosphorus adsorption curves on all studied soils and according to Giles classification compared to the curves of the adsorption, is class (S), form figure 9 can be inferred from this type the presence of phosphorus adsorption, but in very small quantities due to the presence of large gravitational forces between the elements in the solution and the adsorbed surface. [19]

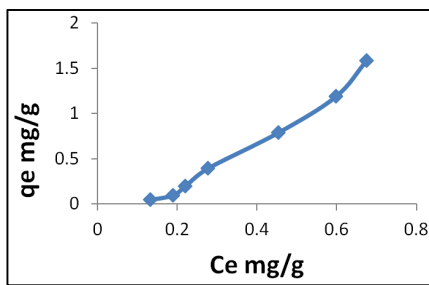


Figure 10. Adsorption Curve of studied soils.

### 3.9. The Effect of Contact Time

Figure 10 shows that the amount of adsorbed phosphorus on the surfaces of the soil increases with increased time until it reaches its maximum value after 40 minutes and then remains constant until after 60 minutes and this confirms the arrival of the adsorption process to a state of equilibrium. The equilibrium time for each soil of the region under study was determined by drawing the relationship between the time on the horizontal axis and the amount of adsorbed phosphorus on the vertical axis, some soils (Tasawa, Dojal, Tokroten) showed a marked variation of the  $q_e$  values between the contact time (10-60) minutes, while the rest of the soil showed convergence in the values ( $q_e$ ) for all the applicable contact times.

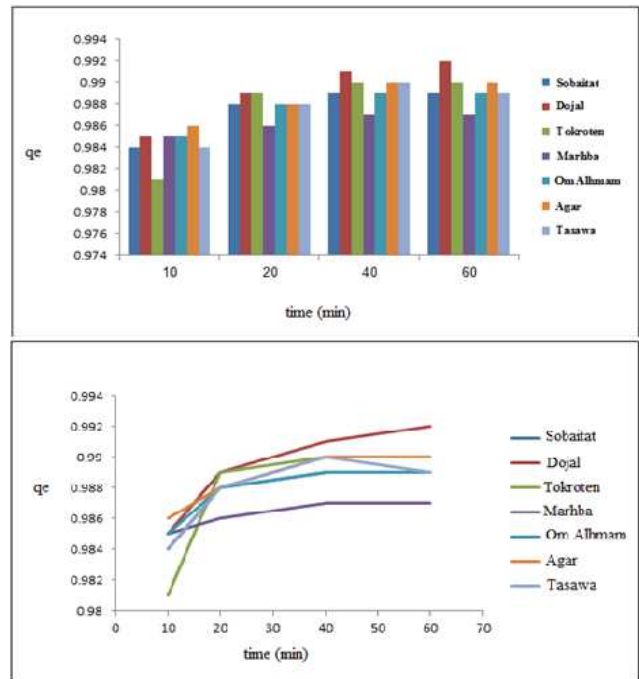


Figure 11. Correlation of time and the amount of phosphorus measured in the soil.

### 3.10. Application of Adsorption Models

The adsorption models of Freundlich and Longmire have been applied. in comparison with the correlation coefficient and the standard error, the Freundlich model was distinguished by the best description of phosphorus adsorption in all the soils studied in order to give the lowest standard error and the highest correlation coefficient.

#### 3.10.1. Application of the Freundlich Model

When applying the Freundlich model to the results, it was found that there was a good match for the adsorption curve for all the soil studied and the correlation coefficient was high, which was likely to be that the adsorption sites uneven in its energy, allowing multi-layered adsorption to occur extensively along the soil surfaces. The soil of Agar had the highest value of the adsorption capacity was recorded (3.946) compared to the rest of the soil studied, as shown decrease in the values of adsorption intensity ( $n$ ) for all soils, as evidence of the ease of release of phosphorus ion from the adsorption surfaces to the soil solution.

Table 2. Constants of Freundlich equation.

	Sobaitat	Dojal	Tokroten	Marhba	Om Alhmam	Agar	Tasawa
Kd	2.876	2.533	1.536	3.449	1.735	3.946	2.212
N	0.503	0.745	0.734	0.480	0.525	0.383	0.691
R <sup>2</sup>	0.959	0.965	0.927	0.985	0.966	0.961	0.970
SE	0.063	0.085	0.119	0.037	0.058	0.121	0.065

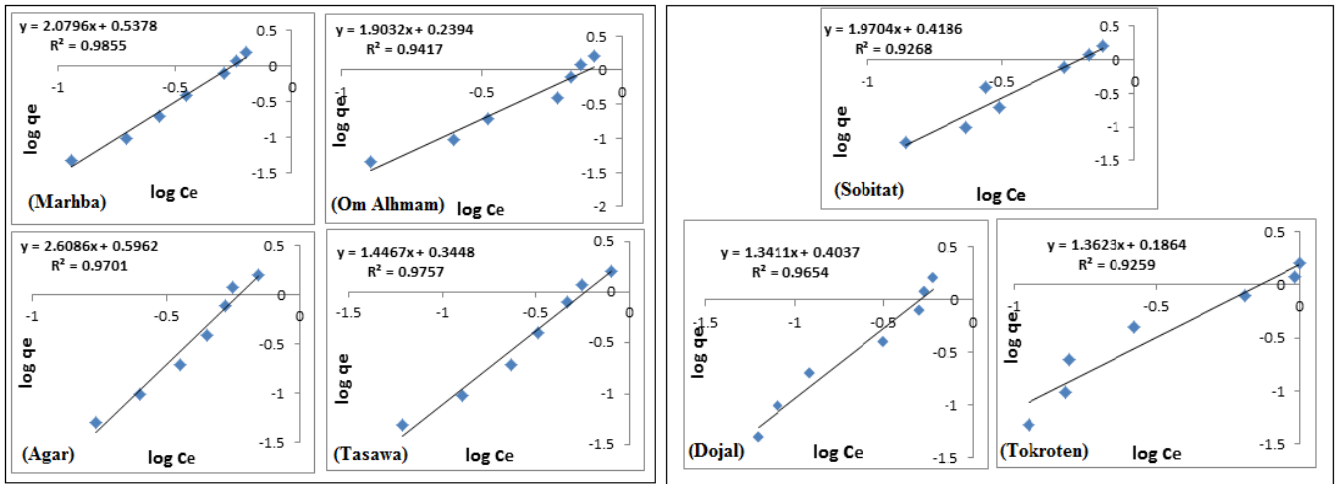


Figure 12. Freundlich isotherms of studied soils.

### 3.10.2. Application of the Langmuir Model

When applying the Langmuir model, it was found that the model did not match with all the soils studied. The values of the adsorption intensity ( $q_{max}$ ) of these soils are small, which is likely to be very weak adsorption.

Table 3. Constants of Langmuir equation.

	Sobitat	Dojal	Tokroten	Marhba	Om Alhman	Agar	Tasawa
B	1.207	0.993	0.612	1.447	1.160	0.771	1.371
$Q_{max}$	0.169	0.492	0.533	0.135	0.106	0.557	0.272
$R^2$	0.625	0.582	0.325	0.675	0.721	0.537	0.772
SE	0.166	0.161	0.351	0.077	0.075	0.188	0.039

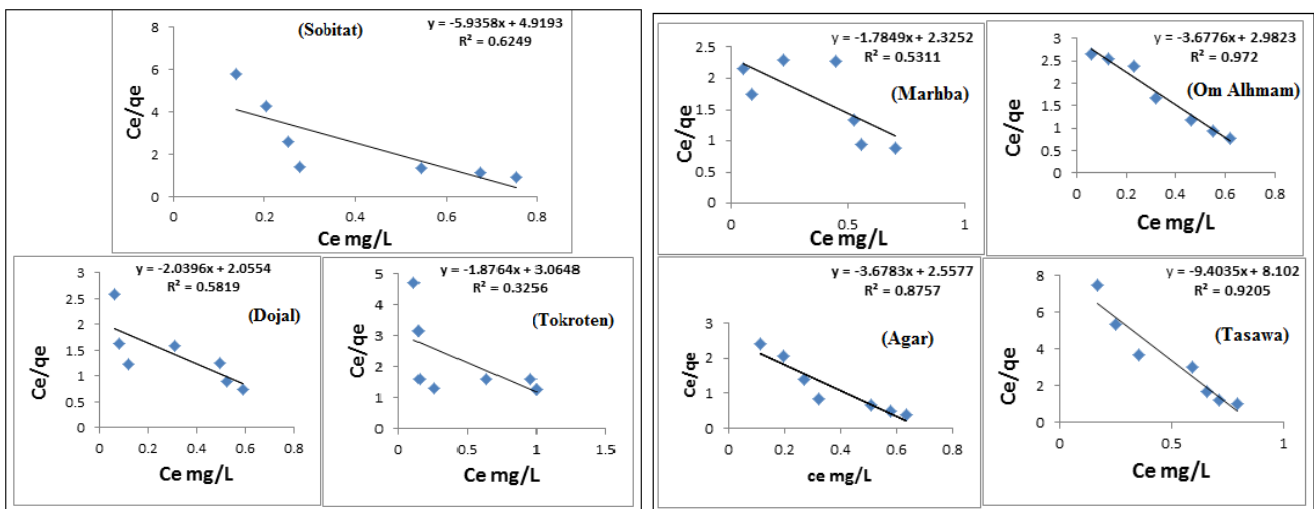


Figure 13. Langmuir isotherms of studied soils.

### 3.10.3. Free Energy for Adsorption

It has been shown that the adsorption free energy values for each soil studied are negative, which confirms the ease of the phosphorus adsorption process on the soil and that the adsorption process has been spontaneous under experimental conditions. And their values are also in line with the adsorption isotherms constant values. The general rule with

regard to the possibility of a spontaneous chemical reaction is that the chemical reaction prefers to move in the direction of the side that leading to a decrease in the value of the free Gibbs energy ( $O > \Delta G^0$ ), which is a natural situation, since most systems tend to be in a direction where energy decreases. The values of free energy change  $\Delta G$  are negative as expected for a spontaneous adsorption process.[20]

**Table 4.** Free energy values compared to Freundlich constant.

	Tasawa	Agar	Om Alhmam	Marhba	Tokrotan	Dojal	Sobaitat
G $\Delta$	12.13-	-13.59	-11.51	-13.25	-11.21	-12.47	-12.79
Kd	2.212	3.946	1.735	3.449	1.536	2.533	2.876

## 4. Conclusions

This study found that the higher the amount of phosphorus intake in most soils, the lower the amount of phosphorus in the soil extract recorded after equilibrium. Also that the amount of phosphorus adsorbed on the surfaces of the soil increases with increased contact time until it reaches its maximum value after 45 minutes and then remains constant until the end of the experiment (after 60 minutes), confirming the arrival of the adsorption process in the state of equilibrium. The results showed that the phosphorus adsorption isotherms on all the soils studied was similar to the type (S) according to the Giles classification, as it was found to follow the Freundlich adsorption equation. The negative free energy ( $\Delta G$ ) values confirmed the ease of the phosphorus adsorption process and that the adsorption process was spontaneous under experimental conditions. The constant effect of "Kd" on free energy values ( $\Delta G$ ) was also observed.

## 5. Recommendations

Based on the results obtained through this study, we recommend:

1. In the absence of studies on these soils, further experiments on the soil of these areas are recommended in order to know the extent to which these soils are capable of processing plants with phosphorus and to develop an appropriate and economical fertilizer plan for such soils.
2. Irrigation periods should be increased when phosphate fertilizers are added, as the binding strength is very weak and the release of phosphorus is easy.
3. Do not mix phosphorus fertilizers with soil because increasing the mixing increases the amount of phosphorus installed and preferably adds fertilizer around the plant.
4. When using any type of salt water in agriculture, it is necessary to double the batches of phosphate fertilizers added to the soil or to use it in accordance with the composting recommendations adopted by agricultural extension centers or other agricultural departments and to educate farmers on this important point in agriculture.
5. Biological experiments are recommended to determine the impact of organisms on phosphorus soil content.

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