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## The adsorption of phosphate by soils rich in palygorskite in the oasis of Alhassa Saudi Arabia

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### **Abstract:**

Phosphorus sorption by calcareous and gypsiferous soils rich in palygorskite has been studied. The P adsorption was measured at 0-60  $\mu\text{g ml}^{-1}$ . Most soil samples showed a high affinity for P sorption at low solution concentrations. At higher P solution concentration, P sorption was accompanied by a change in the slope of the isotherms. The higher P, the lower pH values were gained. The reduction in the final pH was related to the amount of P sorbed. The reference palygorskite showed only a small adsorption capacity for P. This small sorption indicates that palygorskite is behaving in a similar manner to that of a 2:1 phyllosilicate mineral. Since the equilibrium solution background is  $\text{CaCl}_2$ , the adsorption of P by palygorskite is that probably some of the exchangeable site occupied by Ca. The contribution of palygorskite to P adsorption is then small.

### **Introduction:**

Phosphorus (P) is the most important nutrient element (after nitrogen) limiting agricultural production in most regions of the world. It is an extremely chemically reactive mineral. In all its natural forms, including the organic states, P is very stable or insoluble, and only a very small proportion exists in the soil solution at any one time (Holford et al. 1974). In neutral and alkaline soils, P occurs as calcium (Ca) and magnesium (Mg) phosphates and is adsorbed on the surfaces of Ca and Mg carbonates.

Adsorption and precipitation of phosphate has been demonstrated for pure calcite (Freeman and Rowell, 1981) and for naturally occurring  $\text{CaCO}_3$  (Holford and Mattingly, 1975). These authors showed that Fe oxide impurities largely appear to control the sorption of P in soils they studied. In contrast, most studies in calcareous soils, including a wide range of soils derived from limestones (Holford and Mattingly, 1975) Sudanese soils (Hamad et al. 1992) mediterranean soils (Carreira & Lajtha, 1997) Soils and Torrent, 1989) and African soils (Amrani et al. 1999 and Tunesi et al. 1999)

have shown strong positive correlations between P adsorption capacity and active CaCO<sub>3</sub> content.

P adsorption depends on the physical properties and chemical composition of the whole soil system (Matar *et al.* 1992). Curtin *et al.* (1992) reported that P adsorption has been shown to be affected by pH, clay minerals, organic matter content, exchangeable cations, ionic strength of the solution and redox potential. The concentration of P is important in determining the nature of the sorption reaction. According to Olsen and Watanabe (1957), at P concentrations above 180–250 µg ml<sup>-1</sup> adsorption is unable to explain the loss of P from solution. Freeman and Rowell (1981) reported that the critical concentration of P was up to 100 µg ml<sup>-1</sup> above which level precipitation of P occurred. In addition, the most important soil physical property, which is related to the adsorption behaviour of P is the total surface area of the soil particles (Matar *et al.* 1992). A positive relationship between P sorbed and surface area of the soil was found by Arambarri and Madrid (1971).

The initial reaction between P and the soil is a rapid reaction, which subsequently slows down and continues for a long time (Rajan and Fox, 1972). Adsorption isotherms, being fitted using adsorption equations such as the simple or two-surface Langmuir equations, are very often used to describe the initial P sorption by soil (Barrow, 1978). The slower reaction following P adsorption is then assumed to be either a precipitation reaction or a diffusion onto the solid on which the P is sorbed.

Palygorskite is a hydrated magnesium silicate with fibrous morphology and chain structure. It is considered to be different from that of other layer silicates in lacking continuous octahedral sheets. The most important characteristic of this mineral, however, is that it has high porosity and is extremely high external and internal surface area (Singer, 1989). The occurrence of palygorskite at high pH and its association with common soluble salts such as calcite, dolomite or gypsum, links it chemically to the alkaline system. Generally, the study of phosphorus adsorption in soil rich in palygorskite has not been reported in the oasis soils. Therefore, P sorption isotherms were measured for samples rich in palygorskite containing variable amounts of CaCO<sub>3</sub> and gypsum, and for pure palygorskite sample. Our hypothesis is that the presence of zeolitic

channels, micropores and high surface area of palygorskite mineral would affect the adsorption potential of P. The objectives are: To identify and quantify the mineral content in the soil samples and its distribution in the soil matrix, and to study P sorption isotherms on different soil samples rich in palygorskite and its effect on the sorption of P.

#### **Material and Methods:**

Based on the soil classification of the Al-Hassa oasis (Ministry of Agriculture and Water, 1986), the field studies were carried out by digging profile on the the dominant soil type in the study area. Samples were chosen after the preliminary results.

Sample1: Lithic Haplogypsid-uncultivated- subsurface (8-55cm )

Sample2: Leptic Haplogypsid- uncultivated- subsurface (19 100cm )

Sample3: Typic Torriorthent-cultivated- subsurface (5-19cm ).

Sample4: Anthropic Torrifluvent- cultivated- subsurface (84 100cm)

Sample5: Cambic Gypsiorthid-cultivated- surface (0-46cm ).

Soil samples were analyzed for particle size distribution using the hydrometer method (Day, 1965). Soil pH and electrical conductivity were measured in 1:5 soil water extracts. Calcium carbonate was determined using a Bernard calcimeter. Gypsum content was determined by the method described by Bower and Huss (1948). The clay fraction was collected by the sedimentation method. The clay suspension was oriented onto two ceramic tiles and saturated with K and Mg. Mg saturated samples were analyzed by x-ray diffraction (XRD) at room temperature and scanned from 3 to 30 ° 2θ and following glycerol solvation over night they were scanned from 3 to 15 ° 2θ. Potassium saturated samples were scanned from 3 to 15 ° 2θ after drying at room temperature, after heating the samples at 330 °C for two hours and at 550 °C for three hours.

Different component mixtures of standard minerals were prepared and used as external standards. The method of calculation was similar to those described by Brindley (1980) and Reynolds (1989). The ratios of integrated intensities of hkl of various peaks were used to quantify the minerals after comparing the ratios with standard mixtures. The areas under peaks of

various minerals were calculated using a computer program Traces. The peak area was measured for three separate samples and their mean value was used for mineral quantification.

Clay fraction was analyzed for its clay mineral type. Semi-quantification for all mineral present was calculated similar to methods described by Brindley (1980) and Reynolds (1989). A Philips EM400 transmission electron microscope (TEM) was operated at 120 kV to identify the type of clay minerals. Thin sections were made from undisturbed soil clods. All slides were then stained with Alizarin Red S (omitting the etching step due to the presence of calcium carbonate) in order to identify the morphological and distribution of soil minerals in the soil.

Phosphorous adsorption study was conducted using a range of P concentrations (5, 10, 15, 20, 30, 40, 50 and 60  $\mu\text{g P/ml}$ ) in 10 mM  $\text{CaCl}_2$  (Rowell, 1994). Three replicates of 2.5 g air dried soil samples (< 2 mm) were shaken with 25 ml 10 mM  $\text{CaCl}_2$  containing the designated concentrations of P in 50 ml centrifuge tube on reciprocal shaker for continuously 24 hours. The suspensions were then centrifuged at 2500 rpm for 15 minutes and filtered through Whatman No. 41 paper (Rowell, 1994). The pH and P concentration in the supernatant were determined. The P was determined by the molybdate blue method (Rowell, 1994). The amount of P adsorbed was calculated by calculating the differences between initial and final P concentrations.

### Results and Discussions:

Table 1 shows the quantitative mineralogical analyses of the clay fraction and on the whole soil bases. The results of mineralogical analyses indicate that clay fractions (< 2  $\mu\text{m}$ ) contained palygorskite, smectite, illite, kaolinite and chlorite, whereas calcite and gypsum were the most dominant mineral on the whole soil bases. The palygorskite is the most abundant phyllosilicate mineral in the clay fractions of most Al-Hassa soils. Smectite considered the second common mineral in the oasis. Figure 1 shows the TEM photo of palygorskite fibres in the soil sample No 3. Thin section for studied soil samples presented in Figures 2 and 3. Figure 2 shows calcite mineral dominating the soil matrix. The light brown color indicates that Mg replacing Ca in calcite crystal, where the white color indicates the presence

of silica. Figure 3 shows gypsum crystal being indicated by lenticular shape in the pore space.

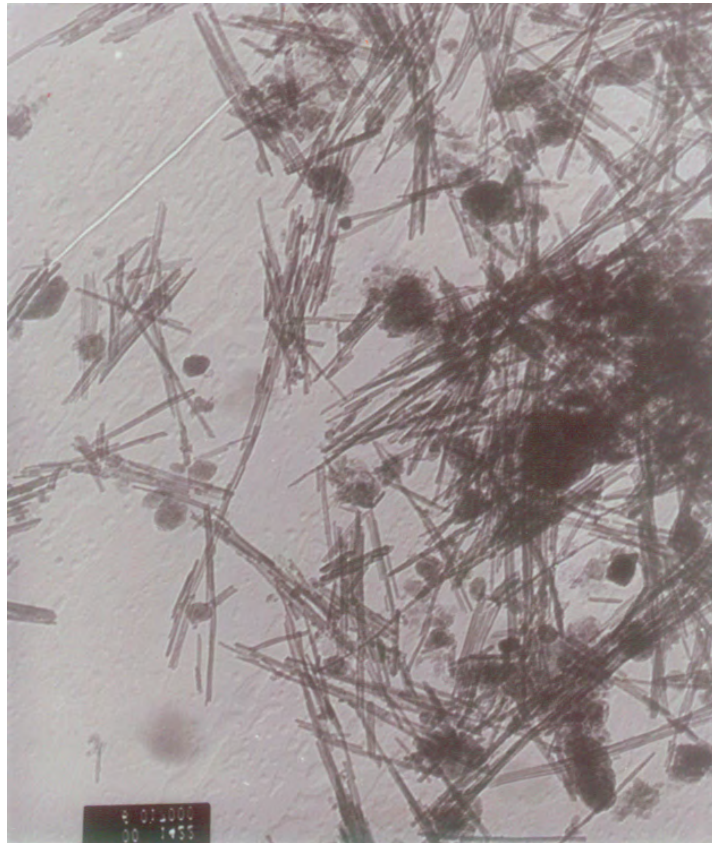


Figure ( 1 )

TEM photo showing the fibre of palygorskite (sample 3).

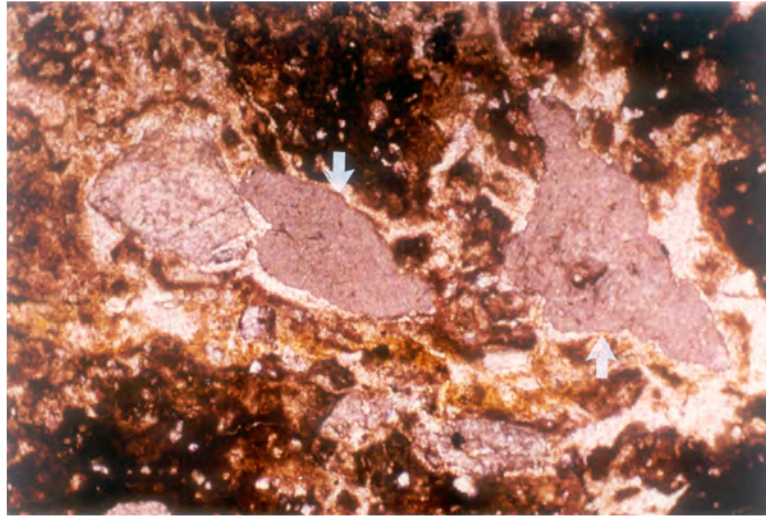


Figure ( 2 )

Optical microscope photo showing calcite mineral, the brown color indicates the calcite mineral where the white arrow indicates Mg-calcite. (X4 sample 3)

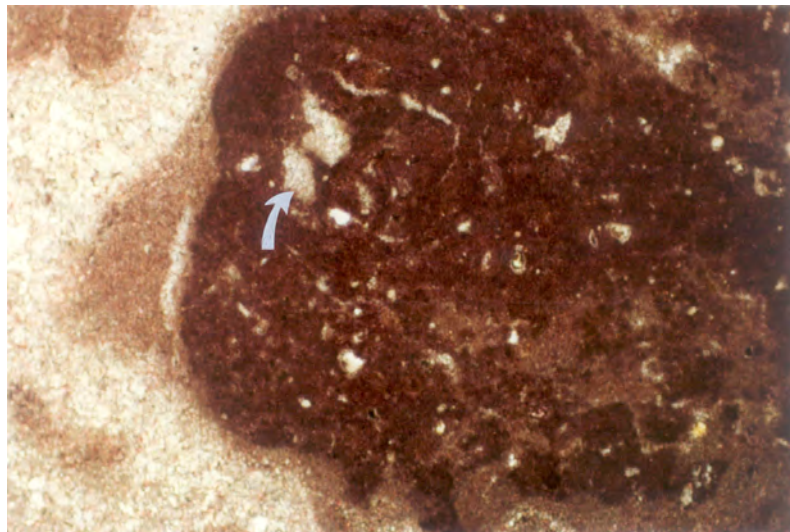


Figure ( 3 )

Optical microscope photo. The white arrows show gypsum crystal (X4 sample 4)

**Table ( 1 )**  
Summary of soil samples properties.

| Soil samples | EC(dS/ml) pH<br>1:5 extr. |     | CaCO <sub>3</sub><br>CaSO <sub>4</sub> .2H <sub>2</sub> O<br>% on the whole<br>soil bases |      | P. | K  | I S Ch Q C<br>% in total clay |    |   |   |    | Particle Size<br>distribution % |      |      |
|--------------|---------------------------|-----|---|------|----|----|-------------------------------|----|---|---|----|---------------------------------|------|------|
|              |                           |     |   |      |    |    |                               |    |   |   |    |                                 | Sand | Silt |
| 1            | 22.4                      | 7.3 | 32.0  | 21.3 | 57 | 9  | 20                            | 6  | 1 | 1 | 6  | 68.0                            | 19.1 | 12.9 |
| 2            | 11.5                      | 7.5 | 26.0  | 0.00 | 55 | 12 | 11                            | 14 | 2 | 1 | 5  | 81.5                            | 8.3  | 10.2 |
| 3            | 6.4                       | 7.1 | 12.6  | 7.1  | 10 | 2  | 4                             | 77 | 0 | 1 | 6  | 92.0                            | 0.3  | 7.7  |
| 4            | 16.0                      | 6.8 | 11.9  | 21.3 | 61 | 9  | 28                            | 0  | 1 | 1 | 0  | 50.5                            | 9.1  | 40.4 |
| 5            | 3.6                       | 8.2 | 30.3  | 0.0  | 54 | 7  | 9                             | 2  | 5 | 1 | 22 | 77.9                            | 6.7  | 15.4 |

Note: P=Palygorskite, K=Kaolinite, I=Illite, S=Smectite, Ch= Chlorite, Q=Quartz, C=Calcite

The P adsorption measured at 5-60  $\mu\text{g ml}^{-1}$ . The adsorption isotherms for the different soil samples are shown in Figures 4. most soils showed a high affinity for P sorption at low solution concentrations. At higher P solution concentration, P sorption was accompanied by a change in the slope of the isotherms. P sorption isotherm for soil samples can be classified as:

- 1) Sample 1 showed the sharpest and the highest P sorption capacity and a reasonable fit to the Langmuir equation, whereas sample 2 the isotherm turn back on its self at 15  $\mu\text{g/ml}$ .
- 2) Samples 3 showed a slower rate and a relatively lower total P sorption capacity than samples 1 and 2.
- 3) Sample4 showed a slow sorption at 5  $\mu\text{g/ml}$  followed by a sharp vertical isotherm and then steady increase with increasing P concentration.
- 4) Sample 5 produced a sharply sloped isotherm at 5  $\mu\text{g/ml}$  followed by a slow sorption isotherm from 10 15  $\mu\text{g/ml}$  that gives a straight line with increasing P concentration.
- 5) Pure palygorskite showed the slowest and the lowest P sorption.

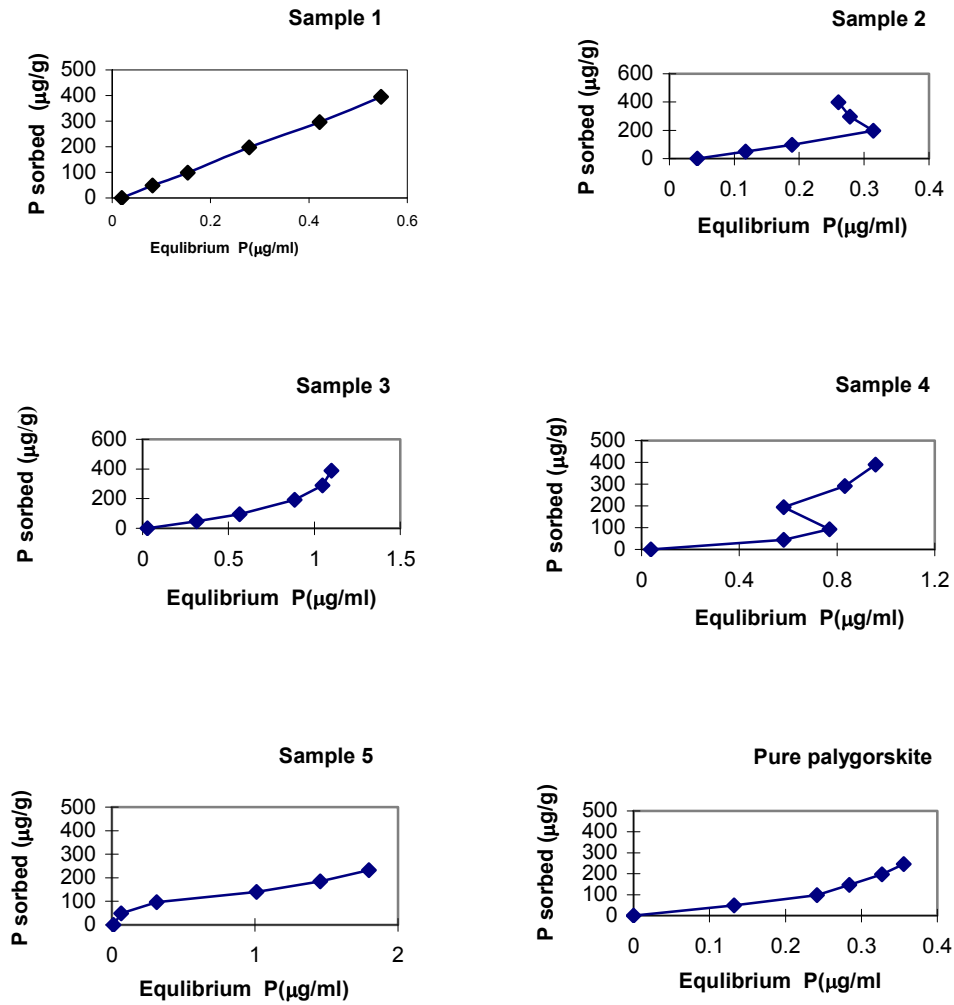


Figure ( 4 ) P sorption isotherms for selected soil samples in 10mM calcium chloride and the pure palygorskite.

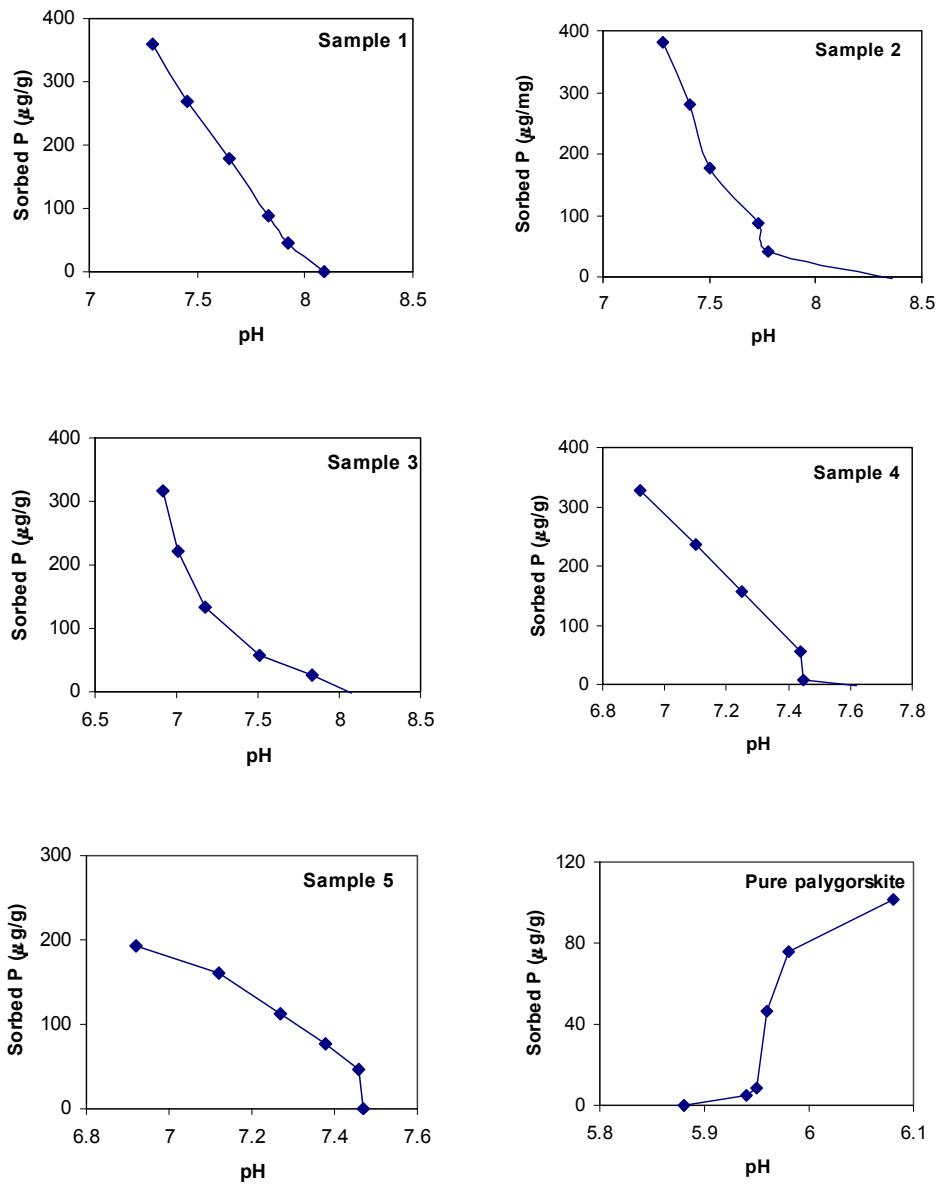


The change in the pH of the system (pH values were measured in the suspensions after the sorption) and added P are plotted and shown in Figure 5. The figure shows that with added P, pH values were reduced. The reduction in the final pH was related to the amount of P sorbed. The small change in pH at low solution concentrations, as found in sample 3, shows that the adsorption was the main reaction between soil and P in solution. This small change in pH was due to the adsorption of  $\text{HPO}_4^{2-}$  and release of H (Holford *et al.* 1974; Xie and Mackenzie, 1990).

The results are in agreement with those of Xie and Mackenzie (1990), who found that for all treatments with added P, the pH values of the suspensions (final pH) were reduced. Their results also asserted that pH and the amount of P sorbed were significantly related. They also concluded that the reduction of pH in the suspension was a result of both P sorption and the precipitation of calcium phosphate.

Table 1 shows the content of calcite, gypsum, palygorskite and kaolinite in the samples tested which may be the cause of high P adsorption for the presence of broken edges in kaolinite and the dominance of palygorskite. As a result of high Ca concentration in these soils (calcareous soil), it is likely that precipitation occurs.

As shown in table 1, sample 1 contained a high gypsum and  $\text{CaCO}_3$  content. The concentration of Ca in this soil is a function of solubility of gypsum and other salts especially the sodium salts in the system. Shariatmadari and Mermut (1999) reported that carbonates are fixed phosphate in soil. Sample 2 is a calcareous soil with no gypsum. This sample contains a high content of palygorskite (55%) and appreciable amounts of montmorillonite (14%) and kaolinite (12%). It is worth noticing that the upper horizons are considered to be gypsiferous (Al-Hawas, 1998). In such a system, mobility of Ca from the upper horizons would dominate the exchangeable sites on the phyllosilicate minerals. In calcareous soils, Ca occupies more than 80% of exchangeable cation sites, and so in these soils precipitation could be the main reaction responsible for the removal of P from solution. However, the low P sorption capacity of sample 5 compared to the other soil samples, may be due to the relatively higher organic matter content decreasing P precipitation (It is surface soil and located in a cultivated area, OM was not determined). The reduction



Figure( 5 ) The relationship between P sorbed and the pH of the suspensions after equilibration for five soil samples and the pure palygorskite.

of P adsorption by organic matter has also been reported by Sibanda and Young (1986) and Anderegg and Naylor (1988). The reference palygorskite showed only a little adsorption capacity for P. Shariatmadari and Mermut (1999) reported that this small sorption indicates that palygorskite is behaving in a similar manner to that of a 2:1 phyllosilicate mineral. The adsorption of P by palygorskite is probably due to the occupation of the exchangeable site by the applied Ca. The contribution of palygorskite to P adsorption is then small.

The high adsorption capacity of soil is probably due to the presence of high concentration of soluble Ca, possibly present as a result of more soluble minerals than calcite such as gypsum. P adsorption in these soils is rapid and occurs at low P solution concentrations, whereas precipitation occurs at relatively high P solution concentrations. Holford et al. (1974) reported that P adsorption is accompanied by only a small change in pH of soil. They claimed that the small reduction in pH of the solution after reaction of  $\text{KH}_2\text{PO}_4$  with the soil may be due to the adsorption  $\text{HPO}_4^{2-}$  from  $\text{H}_2\text{PO}_4^-$  and the subsequent release of  $\text{H}^+$ . At higher P solution concentrations, there is a relatively large decrease in the final pH of the solutions and a distinct change in the slope of the P sorption isotherm. This is also associated with a lack of fit with Langmuir equation, thereby indicating that precipitation is governing the behaviour of P in the soil. Both adsorption and precipitation could happen through the reaction between soil and phosphate (Larsen, 1987). Observation on the precipitation reaction on sample 2 at  $\text{pH} > 7$  could be attributed to the increased retention of  $\text{H}_2\text{PO}_4^-$  at higher level of Ca as explained by Waggon (1987).

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## ادمصاص الفوسفور على ترب غنية بمعدن البيليوجورسكيت من واحة الاحساء (الهلكة العربية السعودية)

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المملكة العربية السعودية

### الملخص:

أظهرت هذه الدراسة القدرة العالية لبعض ترب الاحساء ذات الطبيعة الجبسية و الجيرية و الغنية بمعدن البيليوجورسكيت على ادمصاص عنصر الفوسفور. تعزى التغيرات في منحني ادمصاص عنصر الفوسفور بشكل اساسي الى تباين محتوى عينات التربة من الكربونات و الجبس. والدراسة تبين وجود علاقة عكسية بين محتوى عنصر الفوسفور و درجة الحموضة. أما بخصوص معدن البيليوجورسكيت فوجد أن نسبة ادمصاص عنصر الفوسفور فيه قليلة، و يمكن أن يعود ادمصاص عنصر الفوسفور على معدن البيليوجورسكيت لارتباط هذا العنصر مع عنصر الكالسيوم الموجود في بعض مواقع التبادل البلورية.