

PHOSPHORUS ADSORPTION IN REPRESENTATIVE SOILS OF PESHAWAR VALLEY (NWFP)

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Soil incubation experiment was conducted to study some aspects of phosphorus (P) cycling in soil series of Peshawar Valley. Phosphorus adsorption before and after incubation was studied, physico-chemical properties and AB-DTPA extractable P were determined. Soil samples containing 19 to 22% (w/w) moisture were incubated at 25°C for 7 weeks. The amount of P adsorbed by the soil from KH_2PO_4 solution (0 to 50 $\mu\text{g/ml}$) before and after incubation was calculated by the difference between the amount of P in solution after 24 h shaking and the initially amount was present. These soils contain CaCO_3 , which might adsorb organic P, or form insoluble Ca phosphates. The adsorption isotherm plots highlight the ability of these soils for P sorption. Soil having high amount of CaCO_3 and clay have more affinity for P adsorption in the soil system.

Key words: Phosphorus, Adsorption, Isotherm, Langmuir, Freundlich.

Introduction

The significant role of phosphorus (P) in sustaining soil fertility has long been recognized. In spite, of the marked advancement in our knowledge about P behaviour in soil, understanding about P dynamics in the soil-water-plant system is still far from completion. The P transformation, fixation and release characteristics in the soil-plant system have been the subject of numerous research investigators, (Ansiaux 1977; Sarir 1989; Iqbal 1990,) but in actual practice, the most pertinent issue is to know how much phosphorus can be made available to the growing crop from the native soil pool.

Soils of Pakistan are deficient in nitrogen and nearly 80% of them lack adequate amount of phosphorus to support prosperous agriculture (Nasir *et al* 1990). Some of these soils are inherently deficient in phosphorus due to peculiar nature of parent material (lacking of P bearing mineral, apatite) while others have been made deficient due to mining of this element through intensive cultivation of high yielding crop varieties with no or little P replenishment in the form of inorganic or organic fertilizers, farm yard manure and crop residues for decades. Still in some soils though P contents are adequate, their specific characteristics such as high pH and CaCO_3 content hamper its availability to crop plants. Moreover, in contrast to nitrogen no addition of P through natural biological means takes place. Thus a great majority of soils need extraneous supplementation of P, in order to sustain crops yields.

In Pakistan, the annual use of phosphatic fertilizer has reached approximately 0.4 million tons, against nitrogen, which is 1 million tons (Iqbal 1990) and 551.1 N tons against 2087.6 N tons (Agriculture Statistic of Pakistan 1998). This indicates that the use of phosphorus in relation to nitrogen in the country is imbalanced with nitrogen phosphorus ratio of 3:1, against the required ratio of 1: 1 or 2:1 for most crops. In addition, the phosphatic fertilizers are highly inefficient and the crop plants can make use of only 15 - 25% of the applied phosphatic fertilizers. A significant part of the phosphatic fertilizer is lost through different mechanisms, of which both chemical and biological transformation into insoluble nonavailable form play an important role. In order to maximize the fertilizer phosphorus use efficiency and to know mechanism responsible for P solubility and insolubility, understanding the different aspects of Phosphorus transformation in the phosphorus cycle is important.

Phosphate sorption capacity is an important soil characteristic that affects the plant response to phosphate fertilizer application. Phosphate sorption isotherms have been used to estimate phosphate requirement and to evaluate the residual effects of phosphate fertilizers (Sarir 1989). The inclusion of this parameter with other soil P test may improve the accuracy of the estimate of P fertilizer requirements for optimum crop yield. In the present study, adsorption maxima and bonding energy constants of some selected soils were determined. Such study will give useful information on the adsorption capacity of these soils and will help in the judicious use of phosphatic fertilizers for growing agricultural crops.

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Materials and Methods

The different soil series were identified with the help of Soil Survey Staff (1967). Soil samples of Tarnab, Mardan and Warsak soil series in NWFP were collected up to 20 cm depth for these studies. A composite sample was prepared from five sub-samples taken from the same soil series. The samples were labelled and brought in sealed plastic bags to the laboratory at the earliest and spread out on clean plastic sheets. Any vegetation, roots, stone etc were discarded. The samples were partially air-dried to permit sieving through a 2 mm sieve with minimum disturbance. Precautions were taken to minimize any chemical and biological changes in the samples during the preparation process e.g drying of samples were made at low temperature (possible room temp.) and they were kept away from chemical containing phosphorus. The sieved samples were thoroughly mixed and refrigerated in tied plastic bags until they were to be used for further experimentation.

Soil analysis. The sieved soil samples were analyzed for various physico-chemical properties. Soil texture was determined by hydrometer method. A 1.0 N NaOH solution was used as dispersing agent as described by Moodi *et al* (1959). The pH in 1:5 soil water suspension was determined with the help of pH meter using the method outlined by Richards (1954). Electrical conductivity (EC) in 1:5 soil water suspension was determined with the help of electrical conductivity meter by using the method of Richards (1954). Alkaline earth carbonate was determined by using acid neutralization methods as outlined by Black (1965). Organic matter was determined by the method of Jackson (1958) and moisture was determined by the method of Atkinson *et al* (1958). AB-DTPA extractable P were determined by the method of Soltanpour Schwab (1977).

Incubation procedure. Soil samples were incubated for 7 weeks using the incubation techniques of Jenkinson and Powlson (1976) with some modification. The 120 g soil sample on oven dry basis from each soil were weighed in eighteen plastic vessels 6 cm in diameter, and 10 cm deep. The soil moisture was kept at field capacity leveled by the addition of distilled water. The soil containers were then placed in 1.5 liter kilner jars. The kilner jar lids were then screwed on to make it air tight. The soils were incubated at 25 °C for a period of 7 weeks. To keep the moisture percentage constant, the distilled water was added to the containers at weekly intervals (readjusting any loss in the weight of the soil). Fresh air was also allowed to enter the kilner jar for 10-15 min.

Adsorption procedure. To obtain data for an adsorption isotherm, 5 g oven dry equivalent fresh soil samples were weighed in 250 ml flasks, 50 ml of solution containing 0,5,10,20,30, 40 and 50 µg P/ml were added to these flask. Two

to four drops of toluene were added to flasks to stop microbial activities if any in the soil solution. The flasks were then tightly sealed and equilibrated by shaking on a rotating plate form shaker for 24 h at room temperature. Following the equilibration, the solution was centrifuged and filtered. A control set of phosphorus solution having the same concentration (0-50 µg P/ml) was also run, for measuring the initial phosphorus content in the solution. Aliquots of the clear filtrates and control solutions were analysed for phosphorus using spectronic 601 Spectro Photometer by the method of Watanabe and Olsen (1962).

Results and Discussion

Physico-chemical properties. The physico-chemical properties of the soils series used in this study are presented in Table 1. The pH values of all soil series were neutral (pH 7.2). The organic matter content was low and varied between 0.71 to 0.91%. All the soil series analyzed were found to be calcareous, with CaCO₃ content ranging from 7.32 to 24.76%. Tarnab soil series contained highest calcium carbonate (25%), while Mardan had the lowest (7.32%). Electrical conductivity of the soils generally ranged from 0.24 to 0.32 dSm⁻¹. The percent clay of the most soil series ranged from 9.20 to 33.20 (clay loam to loam).

Ammonium bicarbonate extractable P (later called, extractable P) ranged from 0.58 to 4.15 mg P/kg soil, in which Tarnab soil series had the lowest P (0.58 mg P/kg soil), while Warsak soil series had the highest extractable P (4.15 mg P/kg soil) Table 1. Because of convenience in use and due to the absence of any better alternative chemical extractants are widely used for testing the available P status or the P supplying power in the soil.

Phosphorus adsorption. The graphical plots of the amount of phosphorus adsorbed by the soil against the equilibrium solution concentrations were also plotted in the form of the Langmuir and Freundlich isotherm equations. Adsorption isotherms, Langmuir and Freundlich plots are illustrated in Fig 1-3, 4-6 and 7-9, respectively. Phosphorus adsorption constants calculated from Langmuir and Freundlich plots are given in Table 2.

Adsorption isotherm illustrated in Fig 1-3, indicate that each soil exhibited different adsorption characteristics. The great variation in P adsorption by different soils have important bearing in soil test crop response correlation studies. It seems that both clay initial P and CaCO₃ content play important role in P adsorption by these soils as were seen from adsorption isotherm plots. Phosphorus adsorption was higher in Tarnab soil than in the Mardan and Warsak soils, this probably owed to the presence of more CaCO₃ and clay content in the former

Table 1
Physico-chemical properties of soils used

| Soil series | AB-DTPA extractable P mg/kg | pH* | EC* dSm ⁻¹ | O.M | Moisture | CaCO ₃ | Clay contents |
|-------------|-----------------------------|-----|-----------------------|---------------|----------|-------------------|---------------|
| | | | | ----- % ----- | | | |
| Tarnab | 0.58 | 7.2 | 0.27 | 0.71 | 22.78 | 24.76 | 33.20 |
| Mardan | 1.18 | 7.2 | 0.24 | 0.91 | 19.72 | 7.32 | 9.20 |
| Warsak | 4.15 | 7.2 | 0.32 | 0.91 | 22.05 | 11.88 | 14.40 |

* Soil pH and EC were determined in 1:5, soil, water extract.

Table 2
Phosphorus adsorption constant for some soil series of NWFP calculated for Langmuir and Freundlich plots

| Soil series | Langmuir plot | | | Freundlich plot | | |
|-------------|---------------|-----------|----------------|-----------------|-------|----------------|
| | b µg/g | K L/mg | R ² | Intercept | Slope | R ² |
| Tarnab-BI | 500 | 0.200 | 0.46 | 1.66 | 0.85 | 0.99 |
| Tarnab-PI | 500 | 0.200 | 0.51 | 2.06 | 0.79 | 0.97 |
| Mardan-BI | - | 0.000 | 0.01 | 1.08 | 1.25 | 0.99 |
| Mardan-PI | 1000 | 0.033 | 0.16 | 1.38 | 1.05 | 0.99 |
| Warsak-BI | - | 0.000 | 0.00 | 0.60 | 1.31 | 0.96 |
| Warsak-PI | 333 | 0.100 | 0.68 | 1.41 | 0.77 | 1.00 |

BI: Before incubation, PI: Post or after incubation.

soil. According to Goswami and Singh (1979), the content of clay explains 77% of the variation in P fixation of the soil and it is desirable to determine the clay content of the soil as a routine test for the purpose of recommending the dose of P fertilizers. Phosphorus adsorption was also substantially affected by incubations, and P adsorption was greater after incubation than before incubation in all soils. However, the effect was greater in Tarnab soil which contains low initial P, as compared to Mardan and Warsak soils, which generally contain more initial P.

Generally, an adsorption isotherm is a curve relating the amount of a substance adsorbed at an interface to its concentration at equilibrium in the medium in contact with the interface. Phosphate retention increased linearly with increasing P concentration or addition. Mean P retention by the soil was 80 ± 3% of added P (Agbenin 1998). However, the adsorption isotherm obtained in Fig. 1-3, continued to increase gradually with increasing P concentration, and a well defined maximum is not obtained. Such observations were reported by Bache and Williams (1971) for soils with a concomitant uniform level of bonding energies for P. The data may, however, be treated according to the number of adsorption equations. The data were fitted to the Langmuir adsorption equation:

$$\frac{C}{X/M} = \frac{1}{Kb} + \frac{C}{b}$$

Where C is the equilibrium concentration of phosphate, X/M is the amount of phosphate adsorbed per unit mass. The b is a phosphate adsorption maximum and K is a term relating to the energy of adsorption.

The relationships between values of C/X/M and C were not linear (Fig. 4-6) and as such do not conform to the conventional Langmuir equation. The constants derived from the Langmuir equation in Table 2, indicated great deviation from the linear form of the equation.

The bonding constant, K L/mg, for P adsorption by these soils, calculated from the slope and intercept ranged from 0.03 to 0.2 L/mg with a mean value of 0.13 L/mg, the average value of bonding constant by Rennie and McKercher (1959) was 0.14 L/mg, for Soils ranging in pH from 6.5 to 7.2, while 0.92 and 4.39 L/mg were reported by Olsen and Watanabe (1957) for alkaline and acidic soil, respectively.

The K value, the energy with which P is released, bears an inverse relationship to the maximum P releasing capacity (b value) of soil (Dev et al 1979). The b value of the under study soils ranged from 333 to 1000 µg/g soil Table 2. Different

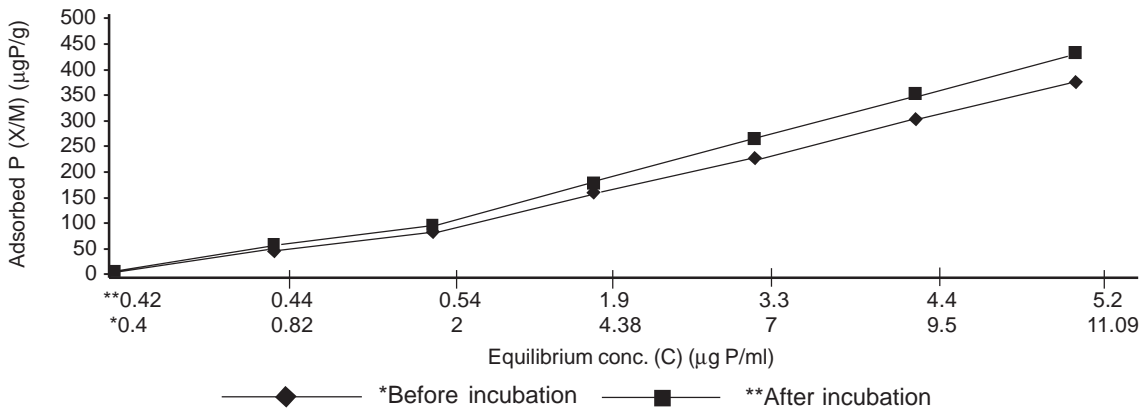


Fig 1. Adsorption isotherm before and after incubation for Tarnab soil series.

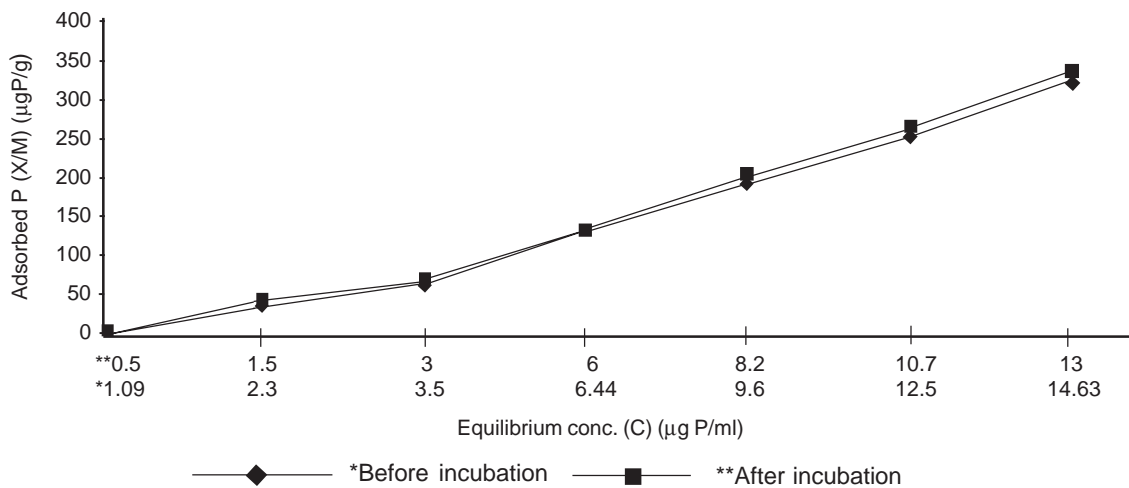


Fig 2. Adsorption isotherm before and after incubation in Mardan soil series.

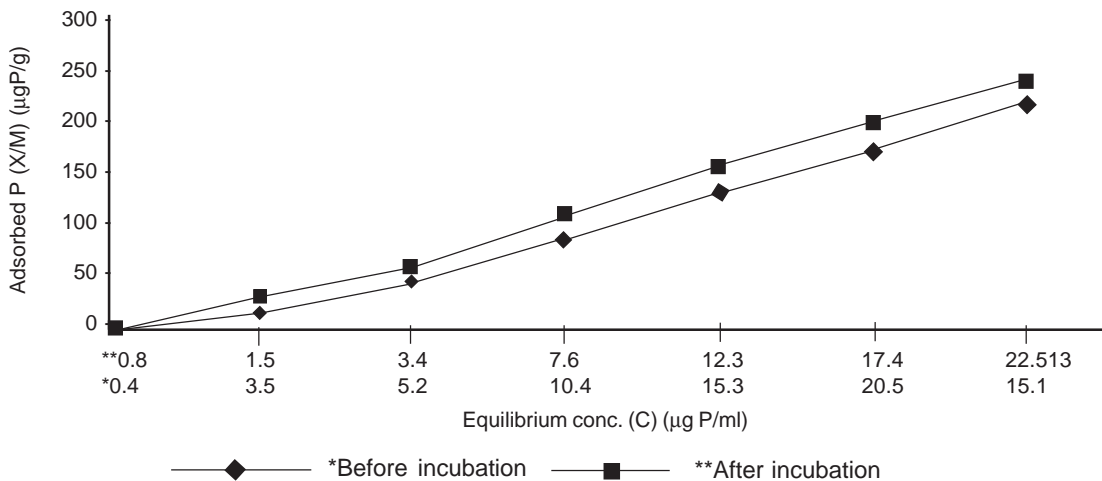


Fig 3. Adsorption isotherm before and after incubation in Warsak soil series.

values of adsorption maximum have been reported by different workers. Sarir (1989) reported as much as 1800 µg/g soil adsorption maximum for Scottish soil, with pH ranged from 3.0 to 7.2. Olsen and Watanabe (1957) found the

adsorption maximum ranging from 105 (alkaline) to 300 (acidic) µg/g soil. The maximum phosphorus releasing capacity reported by Dev *et al* (1979) for different Indian soils ranges from 16-900 µg/g. It is assumed that one hec-

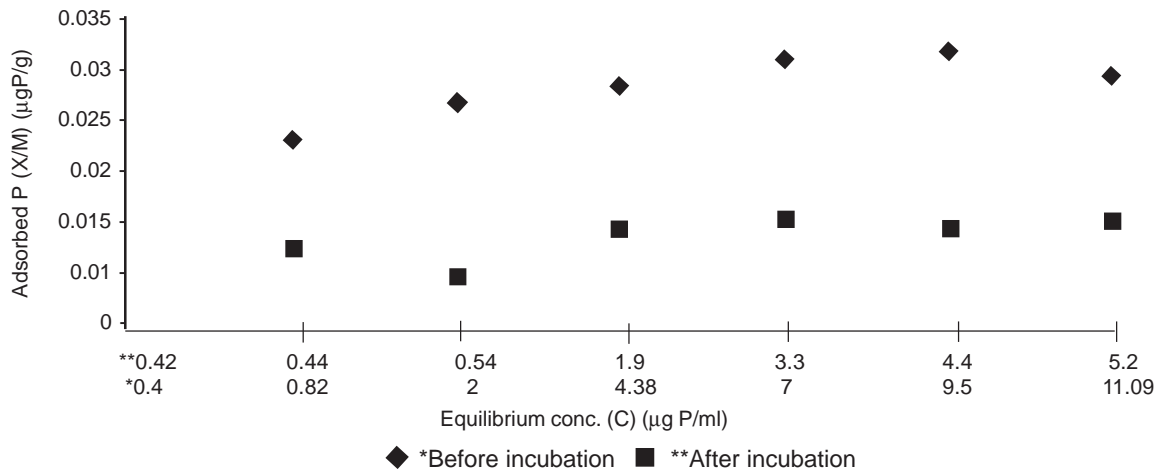


Fig 4. Langmuir adsorption isotherm before and after incubation in Tarnab soil series.

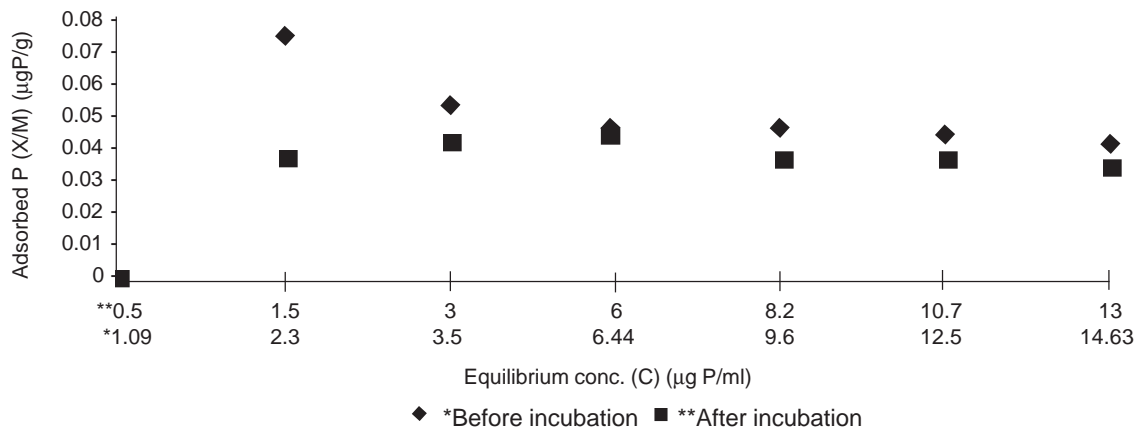


Fig 5. Langmuir adsorption isotherm before and after incubation in Mardan soil series.

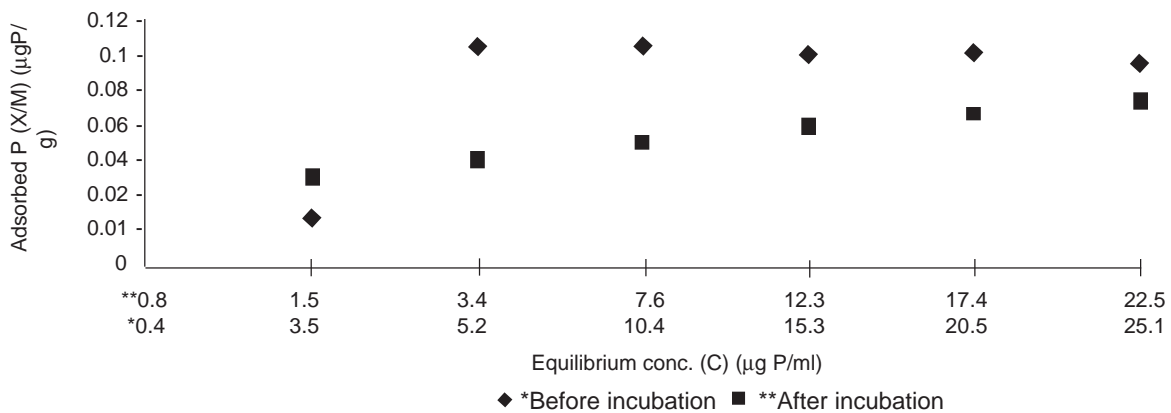


Fig 6. Langmuir adsorption isotherm before and after incubation in Warsak soil series.

tare contain 1800 tons of soil, an equivalent value of adsorption capacity of 0.54 to 1.0 ton P ha⁻¹ can be expected in these soils. However, these constants are markedly affected by experimental errors, and little weight can be

placed, if the experiments are not correctly tackled (Rennie and McKercher 1959). Therefore, considerable work is needed for selecting the concentration at which to measure the isotherm slope, within convenient experimental

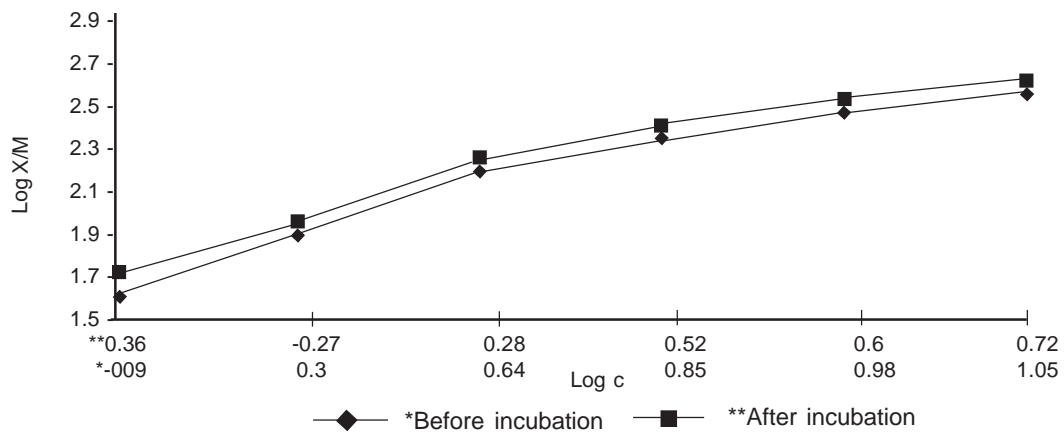


Fig 7. Freundlich adsorption isotherm before and after incubation in Tarnab soil series.

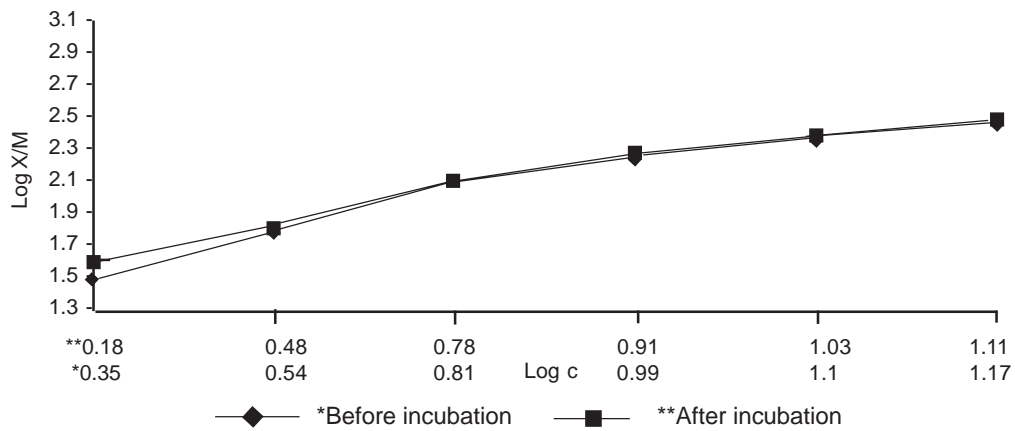


Fig 8. Freundlich adsorption isotherm before and after incubation in Mardan soil series.

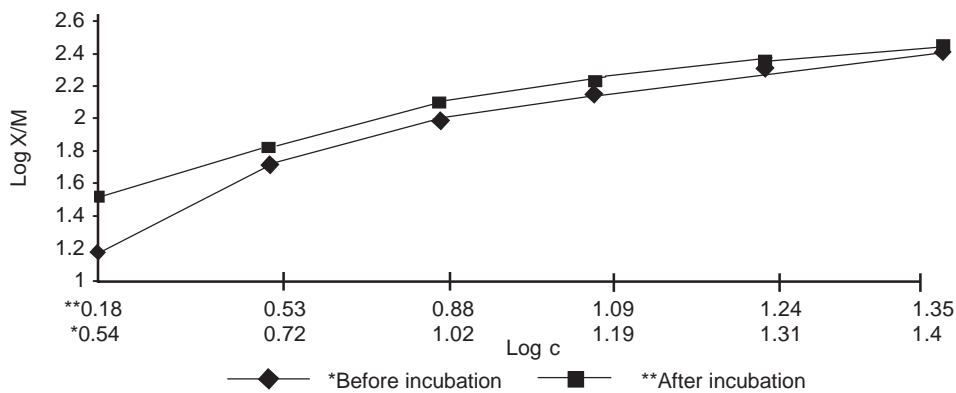


Fig 9. Freundlich adsorption isotherm before and after incubation in Warsak soil series.

range for each soil with different of sorption properties. If data fail to conform to the Langmuir equation, the less demanding Freundlich equation can often be used successfully (Hinrich *et al* 1985). The linear equation is derived as follow:

$$\text{Log } x/m = 1/n \text{ log } c + \text{log } k.$$

Where 1/n is the slope of the regression line, K and n are empirical constant.

Adsorption data were also fitted to the Freundlich adsorption and values log x/m versus log c were plotted. Experimental data proved to obey the Freundlich adsorption isotherm Fig 7-9. Phosphorus adsorption by all three soils (before and after incubation) appeared to conform well to the conventional Freundlich equation and gave a good fit of the linear form of the equation. The fits (R²) of the straight lines to the Freundlich plot are given in Table 2. The R² values indicated a good fit of Freundlich plots.

Castro and Torrent (1998) concluded that the relative significance of Ca phosphate precipitation and P adsorption on variable charge surfaces in calcareous soil varies widely depending on soil properties and amount of P is added. The amount and rate of Ca phosphate precipitation, are related to a certain extent to the amounts of the various soil components, but these relations are far from clear and require further investigation.

Conclusion

It is concluded from the present study that phosphorus adsorption studied in soils before and after incubation did not exhibit a clear adsorption maxima if up to 50 ppm phosphorus solution is added. All the three soils before and after incubation do not follow Langmuir equation but Freundlich equation.

On this basis of the present study, it is not worthwhile to have some recommendation, and further study is needed on phosphorus transformation taking into consideration all aspect of phosphorus cycles e.g respiration rate and enzymatic study alongwith field/pot experiment. Moreover, standardization of method, selection of the extractants, temperature, incubation period, all need a comparative and detailed study.

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