

Impact of Equilibrating Time on Phosphate Adsorption and Desorption Behaviour in Some Selected Saline Sodic Soils

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Summary: To investigate the effect of equilibrating time on phosphate adsorption and desorption on saline sodic soils a study was carried using three soil series from Dera Ismail Khan (Pakistan) district, namely Zindani, Tikken and Gishkori. These soils are alkaline calcareous in nature with greater Electrical Conductivity (EC) and Sodium Adsorption Ratio (SAR) values which classify them as saline sodic soils. The equilibrating time for the adsorption study was 8, 12, 16, 20, 24, 48 and 72 hours for two levels (5 mg L⁻¹ and 100 mg L⁻¹). For desorption study 1, 2, 3, 4 and 5 hours after 24 hours for low and high dilution. Adsorption and desorption isotherms of phosphate were developed for these soils. The Gishkori soil showed the greatest rate of adsorption as compared with the other two soils. Applying Langmuir and Freundlich models to P adsorption data revealed that Freundlich equation ($R^2 = 0.99$) showed a better fit over the Langmuir equation ($R^2 = 0.97$) in the three soils. The desorption curves varied similarly from each other. The amount of P adsorbed was different from that released back to the soil solution. The amount of adsorption increased with the time. Statistical analysis showed that the rate of adsorption for both 5 and 100 mg P L⁻¹ was significantly different at $P < 0.05$ at 16 and 20 hours and at $P < 0.01$ beyond 20 hours. However, the rate of desorption was not significantly influenced by the equilibrating time as compared with the theoretical values of the three series. As the P – desorption curve did not coincide the P – adsorption curve, hence the availability of P to plant was adversely affected on its application.

Keywords: Equilibration time, Phosphate, adsorption, desorption, Isotherm.

Introduction

Phosphate sorption is a process which denotes both adsorption and desorption processes of soil phosphate. In adsorption, the P ions are held on the active sites of the soil particles causing reduction in P availability to plants. The inorganic P however, is continuously moving between the solid phase and solution phase. Desorption is of particular importance in terms of bioavailability to plants.

P adsorption isotherms can be described in quantitative terms as the equilibrium relationship between the amounts of adsorbed and dissolved species of phosphate at constant temperature. Phosphate adsorption isotherms are revealing the action of the P with ions and on oxide. Soil adsorption isotherms are used to measure the capacity of P adsorbed by the soil [1], and are useful in providing information regarding P use efficiency [2] and availability to plants. In alkaline Calcareous soils P availability further exacerbates [3].

Similarly, desorption can be described by a desorption isotherm, which provides the relationship between phosphate on the solid phase and in the

solution phase. This has been referred to as a quantity (P solid) versus intensity (P solution) relationship [4]. The phosphate desorption isotherm is an important characteristic of soil that describes the ability of the soil to release P into solution and make it available to plants. P desorption isotherms can be developed by using the dilution, sequential extraction or anion exchange resin extraction methods [5 and 6]. The rate of desorption from the solid phase is dependent on various factors which includes soil / solution ratio, vigor of shaking, the gradient of phosphate concentration near soil solid phase and temperature [7]. Amongst these factors vigor of shaking is one of the most important factors responsible for adsorption and desorption of phosphate in soil. P retention during the first 0.5 hour is initially rapid after which the reaction slow down [8].

A very little research work has been done on P sorption particularly in saline sodic soils. The aim of the study is to investigate the effect of equilibration time on the phosphate adsorption and desorption in some saline sodic soils. Subsequently the P – availability to plant is affected when P – fertilizer is applied.

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Results and Discussion

Physico-chemical Properties of the Three Soils

The physico-chemical properties of the three soils varied in their properties. The Gishkori soil contains more organic matter, more CaCO₃ and higher electrical conductivity (EC) than the other two soil series. However the extractable Olsen P was found to be greater in the Zindani soil than the Tikken and Gishkori soils (Table-1).

Table-1: Physico-chemical properties of three soil series.

Soil Series	Soil Texture	PH	EC ^a dS m ⁻¹	SAR ^b	CaCO ₃ (%)	O.M ^c (%)	Soil Phosphate (mg Kg ⁻¹)
Zindani	Silty loam	8.31	3.46	15.2	12.58	0.85	7.01
Tikken	Clay loam	8.46	4.35	16.3	13.01	0.93	5.32
Gishkori	Clay loam	8.53	5.59	14.2	15.67	0.99	5.01

^aEC = Electrical Conductivity

^bSAR = Sodium Adsorption Ratio

^cO.M = Organic Matter

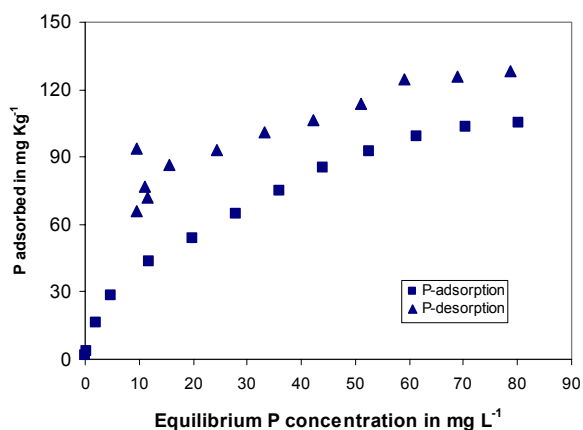


Fig. 1: Phosphate adsorption and desorption isotherm of Zindani soil series.

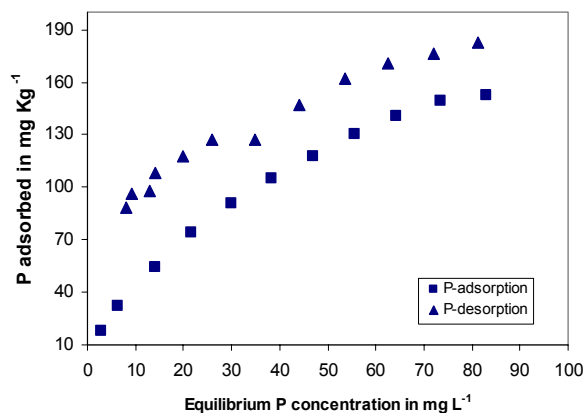


Fig. 2: Phosphate adsorption and desorption isotherm of Tikken soil series.

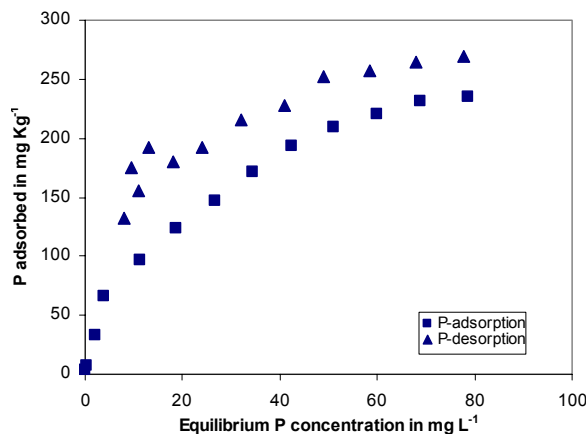


Fig. 3: Phosphate adsorption and desorption isotherm of Gishkori soil series.

Phosphate Adsorption and Desorption Isotherms

The phosphate adsorption and desorption isotherms of the three soils series were determined by plotting the equilibrium concentration of phosphate against the amount of phosphate adsorbed.

The adsorption and desorption isotherms were different due to the difference in the physico-chemical characteristics of the three soils (Fig. 1-3).

In the adsorption isotherms the curves shown were smooth and followed a certain straight pattern. While the desorption isotherm in all the soil series appeared scattered, especially at the initial low concentration. The desorption isotherm showed the greater value for adsorption and the rate of desorption at different equilibrium concentrations appeared higher than the adsorption curves. In all three soils the desorption slope was smaller than the adsorption isotherm. Also the amount of P adsorbed by the soil was more than the amount which was later desorbed i.e. there was a gap between the P adsorption and desorption. The difference in the two isotherms may be due to various factors such as more absorption or penetration of phosphate in to the clay particles, uptake by the microorganisms, pH, organic matter content, presence of soluble and exchangeable salts and soil alkalinity. The rate of P- adsorption in soil increases with a decrease in soil pH due to the interactions between the P source and the charge and electrostatic potential on the surfaces of adsorption [9]. Similarly, in another study a high ($r = 0.83$) correlation coefficient was observed between organic matter content and the amount of P adsorbed and it was concluded that it may have been due to the formation of certain phosphohumic complexes [10]. Other workers have shown that relatively small

amount of exchangeable sodium may significantly influence on the solubility of phosphate [11]. Exchangeable cations, especially sodium, enhances the dissociation and detachment of organic anions, which increases the soluble P concentration due to exchange of Al and Fe complexes [12]. P adsorption – desorption isotherm curves did not meet at the point at which the dilution was not made. There might be two main factors which are responsible for causing the difference. First, P may have become part of the microbial biomass and secondly the phosphate may have continued to adsorb on new exposed sites on clay content of the soil due to more time lag provided in the desorption procedure [13].

Table-2: Regression equations with R² value for three soil series.

S. No.	Soil Series	Model	Equation	R ²
1.	Zindani	Langmuir	$y = 0.0082x + 0.1339$	0.9616
		Freundlich	$y = 0.6082x + 0.3242$	0.9865
2.	Tikken	Langmuir	$y = 0.0046x + 0.1702$	0.9804
		Freundlich	$y = 0.7586x + 0.0498$	0.9913
3.	Gishkori	Langmuir	$y = 0.0037x + 0.0584$	0.974
		Freundlich	$y = 0.6412x + 0.6055$	0.978

Table-3: Comparison of Langmuir Adsorption maximum and binding energy constant for three soils.

S. No.	Soil Series	Adsorption Maximum (b) (mg Kg ⁻¹)	Binding Energy Constant (K) (L (mg P) ⁻¹)
1.	Zindani	121.951	0.0612
2.	Tikken	217.391	0.0270
3.	Gishkori	270.270	0.0633

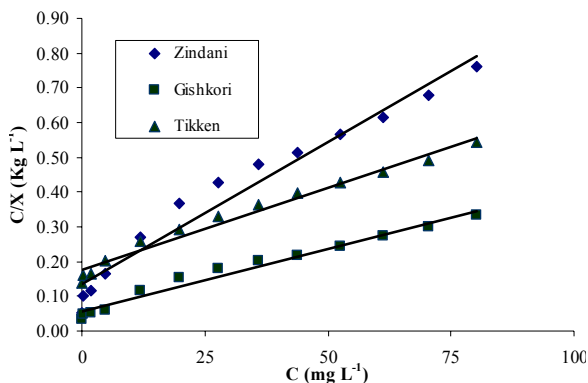


Fig. 4: Langmuir plot for three soil series.

Fitting the Adsorption Data to Different Equations

Fitting the adsorption data to Langmuir and Freundlich equations showed that data was well fitted to both the models. The R² value for Freundlich was highest 0.99 observed in Tikken soil series, while the Langmuir equation having the highest value of 0.980 also observed in same soil series (Table-2).

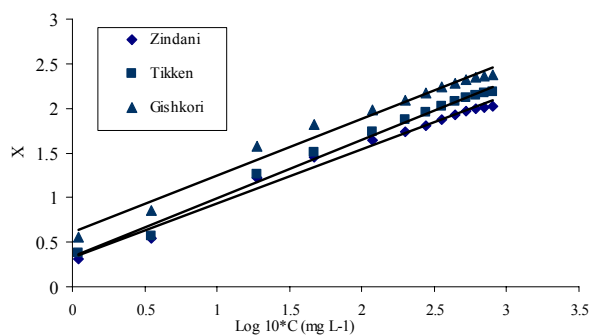


Fig. 5: Freundlich plot for three soil series.

It was also observed from the study that the Langmuir equation well fitted to the data on higher concentration of P. The Comparison of the Langmuir adsorption maximum (b) for the three soil series showed that values of adsorption maximum, was 270.2, 217.3 and 121.9 mg Kg⁻¹ for Gishkori, Tikken and Zindani soils respectively (Table-3). The binding energy was the highest for Gishkori 0.0633 L (mg P)⁻¹, followed by Zindani 0.0612 and 0.0270 L (mg P)⁻¹ for Tikken soil series. The lowest value of the binding energy constant was due to the alkaline nature of soil. Similar results of binding energy constant were reported for the sodic soil [14].

Effect of Equilibrating Time on the Adsorption and Desorption Curves

The effect of equilibrating time on phosphate adsorption and desorption at two concentrations showed different characteristic of the three soil series to adsorption and release of P with the time of contact between soil and phosphate, which was helpful in understanding the behavior of the P adsorption and desorption in soils.

Effect of Equilibrating Time on P Adsorption

(i) On lower concentration of 5 mg L⁻¹

The effect of equilibrating time on P adsorption at the lower concentration of 5 mg P L⁻¹ illustrated that with an increase in time, the rate of adsorption increased. However after 24 hours of shaking the increase in the rate becomes less and the points deviated from linear to a slightly curved shape. Thus, the effect of equilibrating time on the adsorption of phosphate is rapid at the beginning but slows down with passage of time. By applying the t – test of significance, to compare the equilibrating time of different soils, it was found that in the Zindani series, the 12 hours shaking was found non significant compared with the 8 hours. As the time of

shaking increased to 16 hours and beyond significant difference $P < 0.05$ was observed compared to the 8 and 12 hour times (Table-4). A highly significant value ($P < 0.01$) were obtained at 24, 48 and 72 hours in all the three soils. However, Tikken and Gishkori soil series showed highly significant value of P adsorption ($P < 0.01$) reaching 20 hours of equilibration.

Table-4: Effect of equilibrating time on P adsorption at 5 mg L^{-1} in three soil series.

Treatments (Equilibration time in hours)	Zindani Soil	Tikken Soil	Gishkori Soil
	mg P Kg ⁻¹		
8	9.4	16.0	28.3
12	10.7 NS	17.1*	29.8*
16	12.7*	18.6*	31.2*
20	14.0*	18.9**	32.6**
24	15.9**	19.7**	33.7**
48	16.3**	20.3**	33.8**
72	16.7**	21.7**	33.9**

NS Non Significant in column
* Significant at 0.05 level in column
** Significant at 0.01 level in column

Table-5: Effect of equilibrating time on P adsorption at 100 mg L^{-1} in three soil series.

Treatments (Equilibration time in hours)	Zindani Soil	Tikken Soil	Gishkori Soil
	mg P Kg ⁻¹		
8	101.63	153.87	235.9
12	102.48 NS	154.48 NS	236.615*
16	104.14*	156.5*	238.06*
20	105.08**	157.82*	239.84**
24	108.65**	158.19*	241.04**
48	109.49**	159.33**	242.23**
72	110.43**	160.15**	243.98**

NS Non Significant in column
* Significant at 0.05 level in column
** Significant at 0.01 level in column

ii. On Higher Concentration of 100 mg L^{-1}

The effect of equilibration time on P adsorption at 100 mg P L^{-1} on the three soils yielded similar as for the lower P concentration (5 mg P L^{-1}). The time of contact between P and the soil appreciably affected the rate of adsorption. The rate of P adsorption increased in a steady manner.

By applying the t – test of significance time showed a significant effect on the rate of adsorption. The Zindani and Tikken series had initial rates that were non significantly affected by the time of shaking, but as the time of shaking was increased. Beyond 24 hours, the increase in P adsorption was highly significant at $P < 0.01$ in all the soils compared to 8 hours. In Gishkori and Zindani soil series the rate of P adsorption was observed to be highly significant for time at $P < 0.01$ level of significance beyond 20 hours (Table-5).

Similar results of P – adsorption have been reported [15 and 16] where P adsorption in soil

increased with the time of contact. Similarly, the equilibrium concentration of P in the soil decreased with the increase in time [17].

Effect of Equilibration time on P desorption of Soil

The theoretical level of equilibration was calculated for both lower and higher levels of dilution in the desorption studies. The theoretical value for the lower dilution was obtained by multiplying the value of adsorption by 0.833 (50/60), while for the higher dilution it was multiplied by 0.333 (50 / 150). After calculating the theoretical value for each series, P desorption was actually measured by shaking at 1, 2, 3, 4, 5 and 6 hours beyond shaking for 24 hours.

The various treatments of equilibrating time were statistically compared using t – test of significant. The results showed that both lower and higher dilution (Table-6), had a non significant affect on P desorption due to time of equilibration. However, the rate of P adsorption increased at a slower rate after 24 hours of equilibration.

Similarly the higher dilution also showed non significant increase in P adsorption with an increase in time (Table-7.). However, it was observed from the experiment that P adsorption slightly increased with an increase in time.

Experimental

Three soil series namely Zindani (Typic Torrifluent), Tikken (Typic Torrifluent) and Gishkori (Fluentic Haplocambid) were collected from various locations of Dera Ismail Khan and used for the adsorption and desorption studies. The physico-chemical properties including pH, E_c, SAR, O.M. [18] and extractable P [19] for three soil was determined prior to the sorption studies.

Table-6: Effect of Equilibrating time on P desorption with dilution 1:50 – 1:60.

Treatments (Hours)	Zindani	Tikken	Gishkori
	mg P Kg ⁻¹		
	106*	152*	224*
0	106	152	224
1	107	152	225
2	107	152	225
3	107	153	225
4	107	153	225
5	108	153	226
6	108	153	226
	NS	NS	NS

*Theoretical value = Maximum adsorbed x 0.833

In the P adsorption study 13 P concentrations were used including 0.5, 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg P L^{-1} . All the concentration were prepared from a 1000 mg P L^{-1}

stock solution. One gram of air dried soil from each series was accurately weighed in to plastic bottles in duplicate and 50 ml of the respective standard P solutions were added to each bottle.

Table-7: Effect of Equilibrating time on P desorption with dilution 1:50 – 1:150.

Treatments (Hours)	Zindani	Tikken mg P Kg ⁻¹	Gishkori
	43.7*	60.6*	89.5*
0	43.2	60.6	89.6
1	43.6	60.8	89.7
2	43.8	60.9	89.9
3	44.0	61.0	90.6
4	44.2	61.1	91.0
5	44.7	61.5	91.3
6	44.9	62.2	91.7
	NS	NS	NS

*Theoretical Value = Maximum adsorbed x 0.333

Similarly, phosphate desorption study was carried out by taking 0.2 g and 0.5 g of air – dried soil in a plastic bottles in duplicate. Then 10 ml and 25 ml of 100 mg P L⁻¹ solutions were added to respective bottles by maintaining a 1:50 soil solution ratio. All the bottles for P adsorption and desorption were shaken simultaneously on mechanical shaker at room temperature for 24 hours. After removing the bottles from the shakers, the bottles marked for P adsorption were filtered through Whatman No. 42. Phosphate adsorption was based on the formation of Phosphomolybdate complex, which was reduced by using ascorbic acid to produce blue colour [20]. The absorbance was measured by spectrophotometer at wavelength 880 nm. To the P desorption bottles, (marked for 0.5 g soil) were added with 0, 3, 5, 10, 15, 20, 25, 35 and 50 ml distilled water, while 0.2 g soil were added with 25, 50 and 75 ml distilled water were added. The desorption bottles were once again placed on the shaker and were shaken for another 24 hours. The suspensions were then filtered through the Whatman No. 42 filter paper and after adding the reagents to produce blue colour [20] the absorbance was measured at similar wavelength.

The samples were measured using two calibration ranges of 5 – 20 mg P L⁻¹ using the best fit linear calibration with 0, 5, 10 and 20 mg P L⁻¹ standards and of 20 – 100 mg P L⁻¹ using a best fit linear calibration with standard of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg P L⁻¹.

The influence of equilibrating time on P adsorption was determined by shaking 5 and 100 mg L⁻¹ for 8, 12, 16, 20, 24, 48 and 72 hours. Similarly the effect of P desorption was determined at two concentration in soils and calculated theoretically for comparisons.

The P adsorption data for the soils used in this study were fitted into the different adsorption equations.

i. Langmuir equation $C/X = 1/K_L b_L + C/b$ [21]

ii. Freundlich equation $X = K_f C^{1/n}$ [22-24]

where

C = equilibrium concentration of phosphorus in solution (µg P ml⁻¹)

X = mg of P adsorbed (mg P Kg⁻¹)

b_L = Adsorption maximum for Langmuir model (mg P Kg⁻¹)

K_L = Bonding energy constant of Langmuir model (L (mg P)⁻¹)

n = Empirical constant related to bonding energy of soil for phosphate

K_f = proportionality constant for Freundlich model (mg Kg⁻¹)

Conclusion

The equilibrating time influenced phosphorus sorption. The rate of adsorption was significantly increased with the passage of time, while the desorption of P was non – significantly affected by time. It may be concluded that the difference in the adsorption and desorption isotherms were due to the difference in soil properties and the equilibrating time. Langmuir and Freundlich equation showed a good fit to the adsorption data.

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