

## PHOSPHATE ADSORPTION CHARACTERISTICS OF SOME MALAYSIAN SOILS II. RELATIONSHIPS WITH OTHER SOIL PROPERTIES

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*Keywords:* Phosphate adsorption, Characteristics, Malaysian soils, Relationship, Free iron oxides, Organic matter, Silt and clay content.

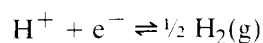
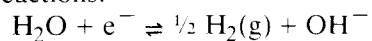
### RINGKASAN

Satu percubaan telah dibuat untuk melihat perhubungan antara kapasiti jerapan posfat yang didapati dari persamaan-persamaan Freundlich dan Langmuir, terhadap sifat-sifat tanah yang lain. Parameter-parameter jerapan yang digunakan ialah Coefficient Jerapan Freundlich (F-a) dan Kapasiti Penimbal Maxima (MBC). Dari analisa korelasi mudah (simple correlation analysis), takat oksid besi dan bahan organan dan kandungan silt + clay didapati ada hubungan secara 'significant' terhadap jerapan-P. Analisa korelasi separa (partial correlation analysis) menunjukkan bahawa pH dan peratus silt + clay memainkan peranan yang paling penting dalam jerapan-P. Tanah-tanah yang dikaji boleh dibahagi kepada dua kelompok dari segi kapasiti jerapan, bergantung kepada kandungan silt + claynya kurang atau lebih daripada nilai kritikal 45%. Dari kajian yang lebih mendalam ke atas kesan pH didapati bahawa tindakbalas antara potensi redox dan pH menentukan pembentukan oksid besi bebas di dalam tanah. Oksid besi kemudiannya mengawal proses jerapan posfat. Persamaan-persamaan yang menghubungkan parameter-parameter jerapan di atas terhadap pH,  $p_e + pH$  dan silt + clay % telah diformulasikan. Satu cara mudah untuk mencari kapasiti jerapan-P telah disyorkan.

### INTRODUCTION

The phosphate adsorption process is controlled by many factors. It is an established fact that in tropical acid soils, the amount of oxides and hydroxides of aluminium and iron which form the major components of soil constituents, play an important role in determining phosphate adsorption characteristics. Nevertheless, it has been shown that other soil properties such as clay content, organic matter content and pH also play their part in the retention of added phosphate. Studies carried out in different part of the world have shown that extractable aluminium and iron oxides, together with organic matter, are significantly correlated with phosphate adsorption (SAUNDERS, 1965). For Malaysian soils, OWEN (1953) showed that pH and clay content affected phosphate retention. AHENKORAH (1968) found that organic matter was one of the dominant factors that correlated with phosphate retention with extractable iron oxides and their interactions with pH. He also found that extractable aluminium and clay content did not give any significant correlation.

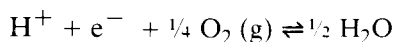
Another essential property which is always overlooked by research workers when relating phosphate adsorption characteristics with other soil properties is the redox potentials. It should be realised that redox potential need not be confined to waterlogged soils only, because most ordinary soils have microstructures and pore spaces in which the states of reduction and oxidation may occur. Redox potential can be expressed in terms of  $p_e$  (- log of electron activity) where  $p_e = E_h/59.2$ . In water saturated soils the pore spaces are filled with water and the diffusion of  $O_2$  (g) is restricted and reducing conditions may prevail. The use of the redox parameter ( $p_e + pH$ ), for describing the redox status of soils has been demonstrated by LINDSAY (1979). Redox status ( $p_e + pH$ ) may be derived from the equilibrium reactions between water and  $H_2$  (g) and  $O_2$  (g) which imposes the redox limits on soils. The reduced redox limit is given by the reactions:



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The oxidised redox limit is given by the reaction:



The equilibrium expressions of these reactions are:

$$K^\circ = [\text{H}_2(\text{g})]^{1/2}/(\text{H}^+)(\text{e}^-) \text{ and}$$

$$K^\circ = (\text{H}_2\text{O})^{1/2}/(\text{H}^+)(\text{e}^-)[\text{O}_2(\text{g})]^{1/4}$$

respectively.

where  $K^\circ$  is the equilibrium constant.

In logarithmic terms the expressions may be transformed into:

$$-\log(\text{e}^-) - \log(\text{H}^+) = \log K^\circ - \frac{1}{2} \log[\text{H}_2(\text{g})]$$

i.e.  $\text{pe} + \text{pH} = \log K^\circ - \frac{1}{2} \log[\text{H}_2(\text{g})]$  for reduced state:

$$\text{and } -\log(\text{e}^-) - \log(\text{H}^+) = \log K^\circ + \frac{1}{4} \log \text{O}_2 (\text{g})$$

i.e.  $\text{pe} + \text{pH} = \log K^\circ + \frac{1}{4} \log \text{O}_2 (\text{g})$  for oxidised state.

Thus ( $\text{pe} + \text{pH}$ ) may be used to indicate the redox state of a soil system, which is directly related to the partial pressures of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$ .

The objective of this paper is to elucidate the interrelationship between selected P adsorption parameters and other soil properties and to examine critically the contribution of relevant properties towards phosphate adsorption and to infer the soil constituent involved.

## MATERIALS AND METHODS

### Soils

The soil samples used represent 12 different sites where field crop trials on grain legumes were established in different areas of Peninsular Malaysia. Composite 0–20 cm samples were collected from each site before the application of any treatment. The soils which differ in their pedogenic origin consist of ultisols, inceptisols and entisols (FOSTER *et al.*, 1979). The samples were air dried and passed through a 2–mm sieve. The silt and clay contents were determined by the Bouyoucous hydrometer method (without destruction of organic matter). Percent

organic matter was estimated by the Walkley – Black Method (results were corrected assuming 77% recovery and % OM = 2 x % C). The pH was determined in distilled water at 1 : 2.5 soil/solution ratio. The redox potential was determined by inserting a platinum/calomel electrode in 1:2.5 suspensions of the soils and distilled water. The suspensions were left open to the atmosphere with intermittent shaking for 24 hours before redox measurements were made (LINDSAY, 1979). Free iron oxides were extracted with sodium dithionite – citrate and the iron estimated by reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  by stannous chloride and then titrating with standard potassium permanganate solution. Extractable aluminium was estimated by extracting with 1M ammonium acetate solution adjusted to pH 4.8 with acetic acid as described by MCLEAN *et al.*, (1958) and determined by aluminon method for aluminium. Exchangeable aluminium was determined in the filtrate after shaking with 1M KCl at 1:5 ratio for 1 hour.

### Determination of P adsorption parameters

P adsorption parameters were estimated by determining the adsorption isotherms and describing them using Langmuir and Freundlich models. The adsorption isotherms were determined using the method of FOX and KAMPRATH (1970). The selected adsorption parameters calculated from the Langmuir and Freundlich models were the Maximum Buffer Capacity (MBC) and the Freundlich adsorption coefficient ( $F-a$ ), respectively. The basis of selection of these parameters has been discussed (AHMAD, 1981).

## RESULTS

### Soil properties related to P-adsorption : simple statistical approach

The values of the adsorption parameters and the measured soil properties are given in *Table 1*. The relationships between soil properties may be first evaluated by simple correlation and the correlation coefficient matrix is shown in *Table 2*. The Freundlich adsorption coefficient and

TABLE 1: SOIL CLASSIFICATIONS, ADSORPTION PARAMETERS AND OTHER SOIL PROPERTIES

Soil No.	Soil Classification	Freundlich Adsorption Coefficient (F-a)	Maximum Buffer Capacity (MBC) ml g <sup>-1</sup>	pH	pe	Exchangeable Al (meq/100g)	Extractable Al (meq/100g)	Free Iron Oxide %	Organic Matter Content %	Silt %	Clay %	Silt + Clay %
1.	Oxic Dystropept	359.58	2163	4.15	10.59	2.80	3.28	3.19	2.6	38	43	81.0
2.	Orthoxic Tropudult	380.29	1726	4.18	9.10	1.85	3.43	1.71	3.0	56	13	69.0
3.	Typic Fluvaquent	211.43	575	4.35	7.60	1.66	2.18	1.20	2.5	36	35	72.0
4.	Typic Fluvaquent	305.87	1873	4.55	10.02	0.55	3.71	3.27	2.6	31	45	76.0
5.	Oxic Dystropept	255.78	966	4.70	10.29	0.70	1.69	2.04	1.7	26	31	57.0
6.	Fluventic Tropopsamment	351.12	2294	5.00	9.21	0.32	1.69	2.11	2.7	21	44	65.0
7.	Oxic Dystropept	436.07	4444	5.25	9.66	0.11	1.47	3.49	3.3	45	30	75.0
8.	Tropaquent	103.07	84	4.48	8.11	0.46	1.29	0.28	1.7	14	18	32.0
9.	Aquic Quartzipsamment	47.99	85	4.63	8.58	0.52	1.28	0.26	1.7	9	10	19.0
10.	Fluventic Tropopsamment	150.52	226	4.93	9.66	0.20	0.43	0.16	1.8	10	18	28.0
11.	Typic Tropopsamment	148.16	220	4.98	7.92	0.34	0.77	1.77	2.3	13	7	20.0
12.	Orthoxic Quartzipsamment	75.47	80	5.05	10.46	0.15	1.77	0.19	1.4	1	6	7.0

TABLE 2: CORRELATION COEFFICIENT MATRIX BETWEEN SOIL PROPERTIES INCLUDING ADSORPTION PARAMETERS

	pe	Excha. Al	Extr. Al	Free Iron Oxide	Organic Matter %	Clay %	Silt %	Silt + Clay %	F-a	MBC
pH	0.11322	0.8518**	0.7015*	0.0481	0.0982	0.4567	0.2132	0.4018	0.1129	0.1349
pe		0.07683	0.3712	0.3712	0.0283	0.0738	0.2947	0.2081	0.3396	0.3604
Exchangeable Al. (meq/100g)			0.6892*	0.2996	0.3342	0.6042*	0.2947	0.5579	0.3775	0.0972
Extractable Al. (meq/100g)				0.6040*	0.5376	0.7230**	0.5535	0.7537**	0.3498	0.3237
Free iron oxide %					0.7732**	0.6820*	0.6989*	0.8363**	0.8311**	0.8322**
Organic matter %						0.8423**	0.4879	0.7904**	0.8829**	0.8302**
Clay %							0.4514	0.8695**	0.8549**	0.6889*
Silt %								0.8332**	0.6543*	0.6287*
Freundlich adsorption coefficient:										0.8956**

\*, \*\* indicate significant levels at P = 0.05 and 0.01 respectively.

Maximum Buffer Capacity are significantly correlated with percentage free iron oxide, organic matter, clay and silt. The correlation coefficient was somewhat improved when silt and clay % were taken together. The pH, redox status and aluminium components do not seem to affect P adsorption in one way or another.

Those properties which seem to affect P-adsorption are intercorrelated with each other rendering interpretations difficult. Partial correlation was thus used to relate the relevant properties with the P-adsorption parameter. The partial correlation matrix is shown in *Table 3*. It can be seen that after adjusting for the level of other soil factors, pH is in fact significantly related to the Maximum Buffer Capacity but not to the Freundlich adsorption coefficient. Furthermore after taking into account the clay and silt content, free iron oxide and organic matter account for no further significant amount of variation in P adsorption. Thus silt and clay % of soils are the dominant components in P adsorption processes.

#### Relationships between adsorption parameters and relevant soil properties: Graphical approach

##### Effect of silt + clay %

The common property that is closely related to both adsorption parameters is the silt + clay %. The soil content of clay and silt is probably a good measure of the number of sites for P-adsorption as it determines the surface area and active sites. The relationship between P-adsorption and soil texture is shown in *Figures 1(a)* and *(b)*. It can be seen that the points can be separated into two

groups based on silt + clay % and adsorption capacities. Since each point represents one soil type the soils under study can be differentiated into two groups; the high P-adsorption and the low P-adsorption groups depending on the silt + clay % found in the soil. The critical percentage of silt + clay is approximately 45%. Soils with silt + clay > 45% have high P-adsorption capacities, F-a and MBC values higher than 180 and 500 respectively, whilst soils with silt + clay < 45% have low P-adsorption capacities.

##### Effect of soil pH

In order to clarify the effect of soil pH on P-adsorption, it is pertinent to examine the relationship between pH and the soil properties which may be involved directly or indirectly with P-adsorption. The most probable soil properties involved in P-adsorption are exchangeable and extractable Al, free iron oxide and the redox status of the soil. The relationships between pH and these properties are shown in *Figure 2*.

Extractable and exchangeable Al decrease with increase in pH (*Figure 2a*). The effect of silt + clay % is also shown in *Figure 2a* which indicates that two separate curves can be fitted correspondingly to silt + clay contents greater or lower than the critical percentage of 45%. The relationship between pH and the redox potential of the soils (pe) is shown in *Figure 2b*. The soils may be divided into two redox status groups irrespective of their silt + clay content, with average (pe + pH) values of 14.79 and 12.79. Soil pH is closely related to free iron oxide content when the results are separated

TABLE 3: PARTIAL CORRELATION COEFFICIENT BETWEEN ADSORPTION PARAMETERS AND SELECTED SOIL PROPERTIES. EACH CORRELATION WAS DONE BY HOLDING THE OTHER SELECTED VARIABLES CONSTANT

	pH	Extractable Al (meq/100g)	Free Iron oxide (%)	Organic Matter %	Silt + Clay %
Freundlich Adsorption Coefficient	0.3448	0.1356	0.1390	0.5185	0.6000*
Maximum Buffer Capacity	0.7662**	0.5104	0.2500	0.4648	0.6896**

\*, \*\* indicate significance level at P = 0.10 and 0.05 respectively.

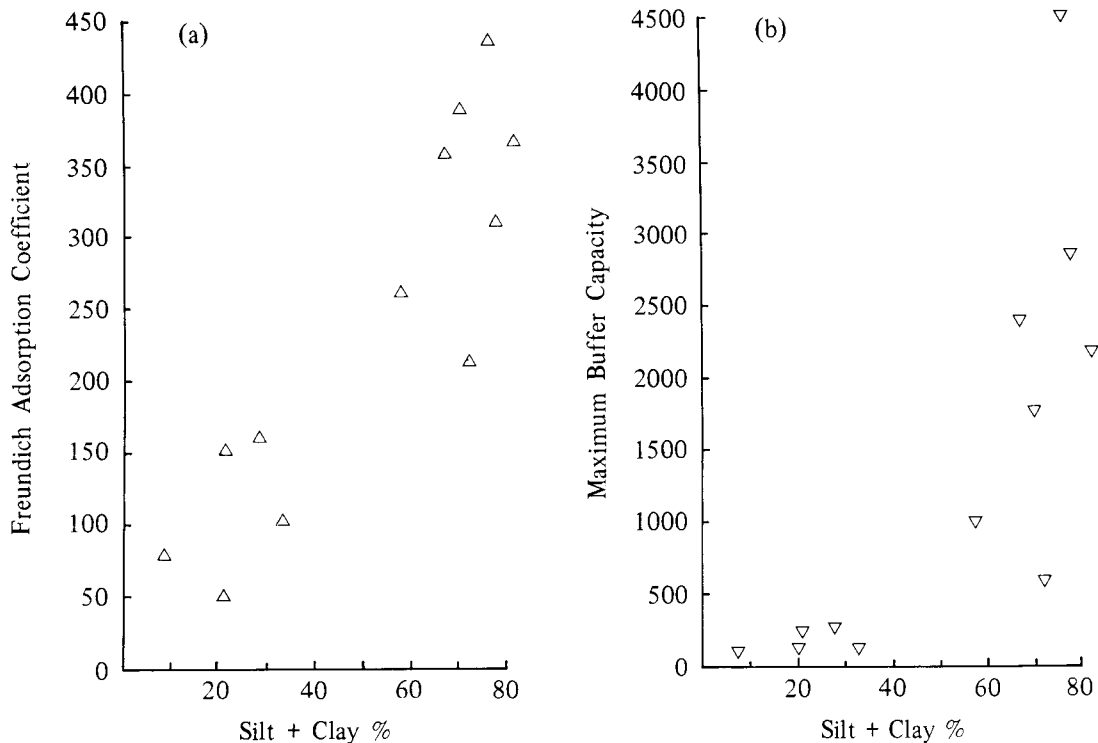


Figure 1: Relationship between  $F-a$  and MBC against silt + clay %

according to these two groups of redox status as shown in *Figure 2c*.

The P-adsorption parameters,  $F-a$  and MBC showed a similar relationship to pH as the free iron oxides (*Figure 3*), when the redox status of the soils was taken into account. *Figure 3* shows that the phosphate adsorption capacity decreased with increase in soil pH and the rate of decrease of the adsorption capacity is higher for soils with lower redox status. This applies both for the Freundlich adsorption coefficient (*Figure 3a*) and the Maximum Buffer Capacity (*Figure 3b*).

## DISCUSSION

From the simple correlation coefficients, it seems that the factors which are important to P-adsorption are the silt and clay content, organic matter and free iron oxides. Soil pH, extractable and exchangeable aluminium which correlate with each other do not seem to contribute to P-adsorption. This is partly in agreement with

the work of AHENKORAH (1968) except that he found no correlation with clay content. The poor relationship with clay content could be due to the important contribution of the silt fraction of soil to P-adsorption as found by this study. For temperate soils, aluminium was found to be the dominant component affecting P-adsorption (WILLIAMS 1959, 1960) and clay and iron oxide showed no significant contributions (SAINI and MCLEAN, 1965).

Using partial correlation, soil pH was found to affect the Maximum Buffer Capacity only, while silt and clay fraction affected both the Freundlich adsorption coefficient and the Maximum Buffer Capacity; the contributions of free iron oxide and organic matter were not significant. The pH affected only the Maximum Buffer Capacity due to the difference in the mode of description of the adsorption capacity by the adsorption parameters. The Maximum Buffer Capacity describes the adsorption isotherm at zero equilibrium concentration, while the Freundlich adsorption coefficient

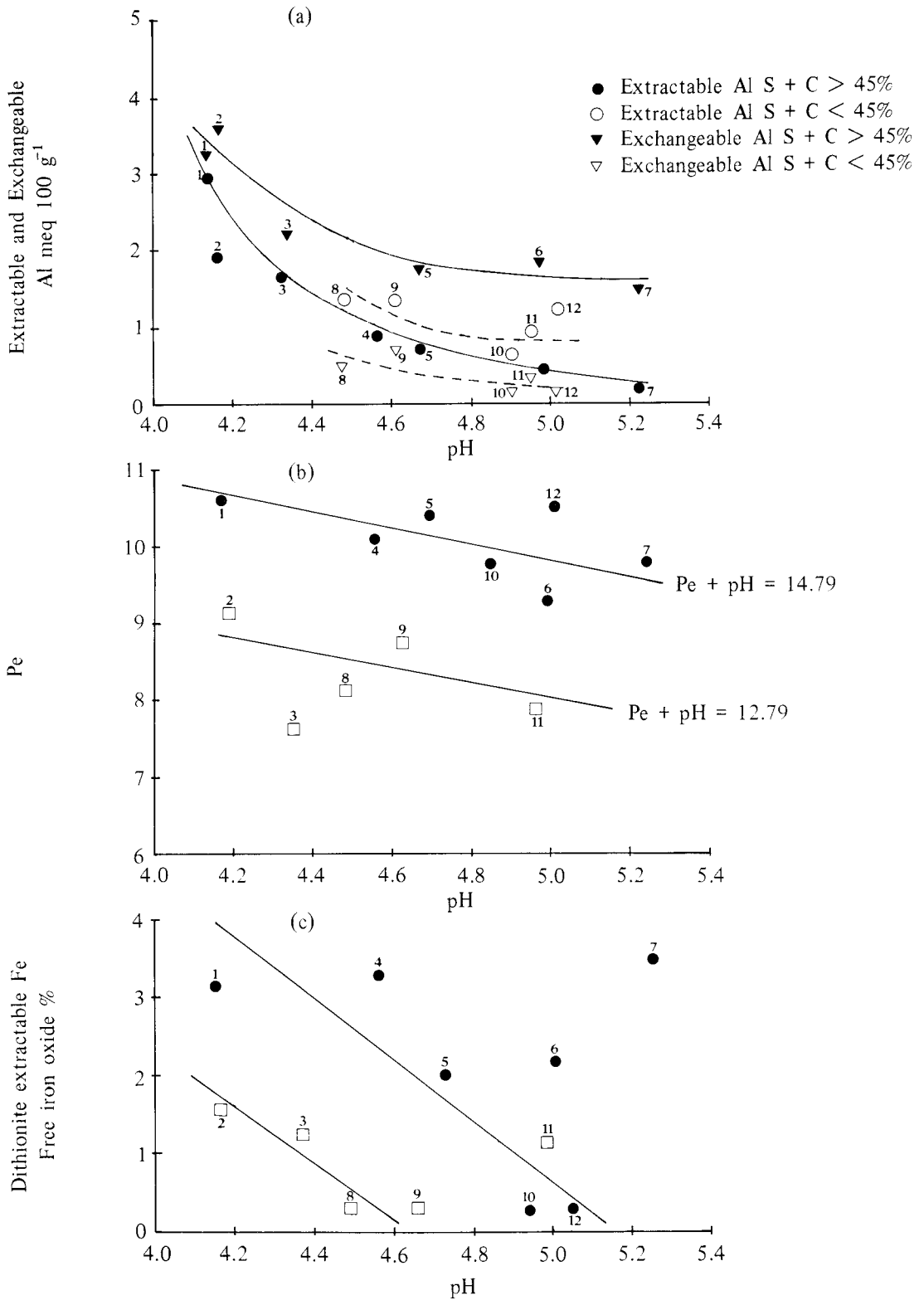


Figure 2: The relationship between pH and other soil properties (Exchangeable and Extractable Al, pe and Free Iron oxide) (S+C) indicates silt + clay. Numbers indicate the soils

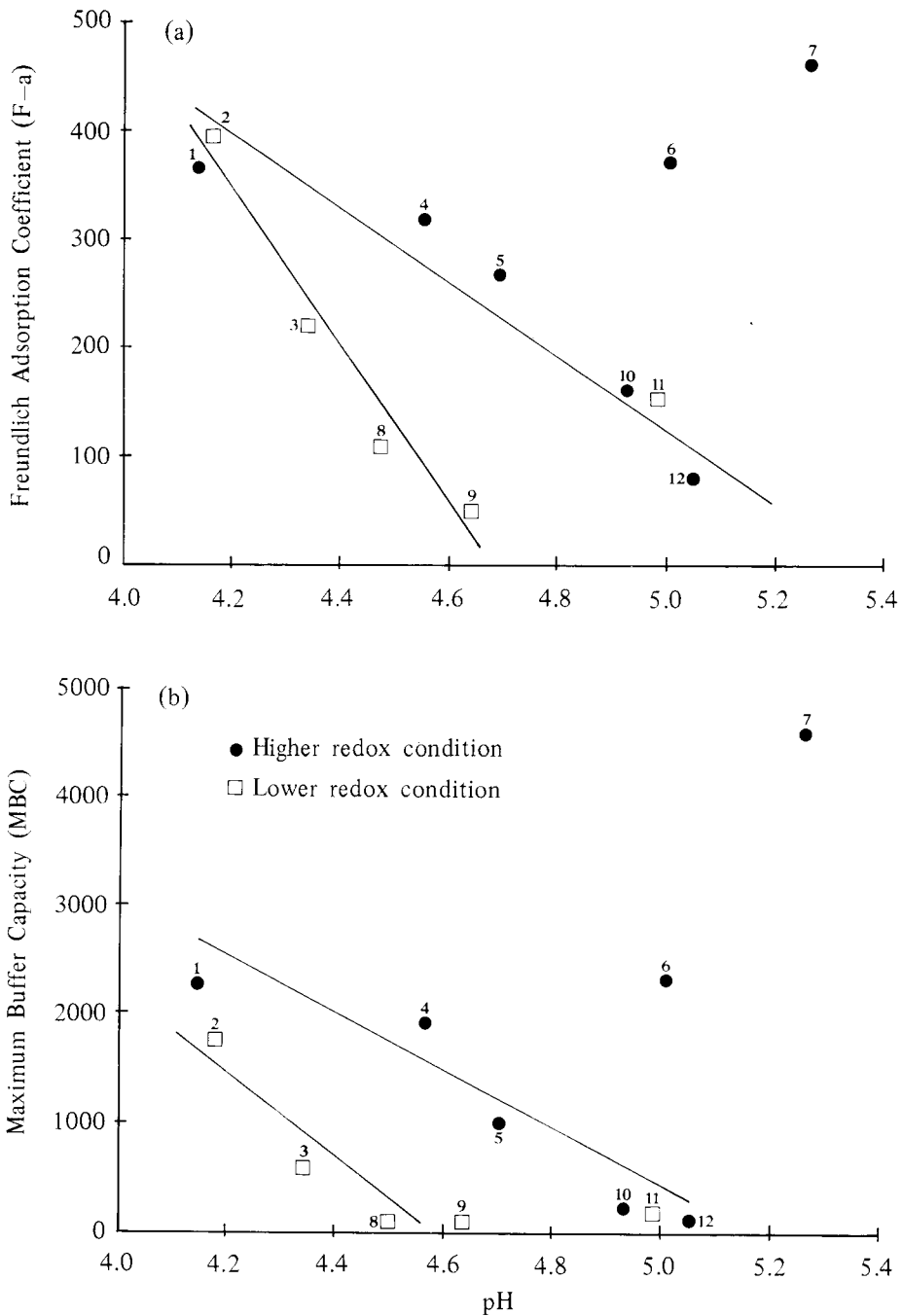


Figure 3: The relationship between adsorption parameters and pH at two different levels to redox conditions. Numbers indicate the soils

describes the entire adsorption isotherm (AHMAD, 1981). A positive correlation indicates that the number of adsorption sites at zero equilibrium concentration is directly proportional to soil pH which could be related to the aluminium saturation of the

surface of soil colloids.

#### Effect of silt + clay on P-adsorption

The silt + clay fraction is the dominant factor in P-adsorption because it provides the surface for adsorption and on which



organic matter, iron and aluminium oxides and hydroxides may be attached. This is reflected by the high correlation between silt + clay and organic matter, iron oxide and aluminium oxide (*Table 2*). In this study the division of soils having high and low adsorption capacity is based on the silt + clay critical value of 45% (*Figures 1a & b*). This division is related to the soil type : soils with silt + clay less than 45% and correspondingly low adsorption capacity are entisols which develop on riverine alluviums; those with silt + clay greater than 45% and correspondingly high adsorption capacity are mainly inceptisols, ultisol and a few entisols (*Table 1*). The entisols in this group developed on old river terraces which showed more advanced soil development.

### Effect of pe and pH on P-adsorption

Soil pH indirectly affects P-adsorption by determining the environment of the adsorption sites. As mentioned above, the components of the adsorption sites are aluminium and iron oxides and organic matter. By examining the behaviour of aluminium and iron as affected by pH (*Figures 2a and 2c* respectively) and comparing it with the relationship between adsorption parameters, F-a and MBC and pH (*Figures 3a and b*), it appears that free iron oxide plays a more important role in P-adsorption than aluminium oxides. This becomes more obvious when pH is coupled with redox potential (pe) of the soil. The relationship between pe and pH (*Figure 2b*) indicates that there are at least two distinct characteristic of redox status of the soils that control the iron activity in soil solution. The transformation of redox associated minerals occurs at fixed (pe + pH) values. This is supported by the two trends of free iron oxides when related to pH, bearing in mind the fact that redox potential can affect solubility and stability of iron oxides in soils.

There are three outlying points in *Figure 2c*. Soil No. 11 which is in the lower redox status. Soils No. 6 and 7 which are in the higher redox status did not conform to the free iron oxide, F-a and MBC trends in

relation to pH (*Figures 2c, 3a and 3b*). This could be explained by the fact that these soils have exceptionally high organic matter content (*Table 1*) as compared to the other soils within each group (soil No. 11 is in the low adsorption groups; soils No. 6 and 7 are in the high adsorption group). Organic matter may lower the redox potential of the soil solution. Another possible explanation is that the iron oxide contents of these particular soils are produced by differential weathering of iron bearing minerals and are not due to the water table history and related oxidation-reduction conditions of each site. It is also possible that at higher pH, aluminium oxides and hydroxides begin to play a bigger role in P-adsorption and mask out the effect of iron oxides and hydroxides. The effect of aluminium is reflected by the low values of exchangeable and extractable aluminium of soils No. 6 and 7 which have high adsorption capacity (*Table 1*).

Drainage conditions may have some bearing on the redox status of the soil. Soils No. 3, 8 and 9 are poorly drained and have lower redox potentials. Under this condition the top soils are susceptible to saturation and pore spaces filled with water and the diffusion of oxygen is restricted and reducing conditions may develop.

### Cumulative effect of pe, pH and silt + clay on P-adsorption

The cumulative contribution of pe, pH and silt + clay % on P-adsorption was subsequently investigated by running the related data (excluding the three soils already mentioned) through a multiple regression analysis taking pe, pH and silt + clay % as independent variables. Without taking into account the effect of silt + clay %, the multiple correlation with respect to MBC and F-a were 0.87 and 0.77 respectively.

The MBC and F-a were extremely well related to the three variables with multiple correlations ( $r^2$ ) of 0.955 and 0.911 respectively. The regression equations are: -

$$\begin{aligned} (\text{MBC}) &= 1444.549 - 1567.200(\text{pH}) + 415.661 \\ &\quad (\text{pe} + \text{pH}) + 15.776(\text{S} + \text{C}) \end{aligned}$$

$$(F-a) = 150.870 - 144.680(\text{pH}) + 40.815(\text{pe} + \text{pH}) + 3.053(\text{S} + \text{C})$$

Where (S+C) is the silt + clay % of the soil.

This implies that the adsorption capacity of soils may be estimated by simple measurements of pH, pe and silt + clay %. The pH component may reflect the proton associated with P-adsorption: the protons being used for ligand exchange of phosphate on the iron or aluminium oxides surfaces (HINGSTON *et al.*, 1972). The negative coefficient of pH indicates that the P-adsorption decreased with increase in pH which conforms to the theory of P-adsorption. The (pe + pH) component governs the redox status of the soil which determines the forms of iron that prevail in the soils. The silt + clay component contributes to the extensiveness of the surface for adsorption. The limitation of using the equations is that the value of MBC must be positive. For this to happen the silt + clay % and (pe + pH) must be exceptionally high so as to provide for a wide range of pH. For example at pH 5.5 and taking the critical value of silt + clay % for high P-adsorption, the (pe + pH) value must be greater than 15.55 in order for the MBC to be positive. The equation involving Freundlich (F-a) gives a wider scope of usage giving a lower limit of (pe + pH) with the same pH and silt + clay %.

Nevertheless, the MBC of the soils used, estimated by the regression equation, are positive when the silt + clay % > 45%. The Freundlich (F-a) values are positive for all the soils used in the study. From preceding section it may also be postulated

that the validity of the equations depends on iron equilibria in soils. When other factors such as organic matter content or aluminium oxides become predominant, the relationship will not longer hold.

## CONCLUSION

Phosphate adsorption parameters were found to correlate significantly with free iron oxide, organic matter % and silt + clay % using simple correlation analysis. With partial correlation, pH and silt + clay % showed significant relationships with phosphate adsorption. It was found that silt + clay fraction plays a direct role in phosphate adsorption in which soils may be grouped as having high and low phosphate adsorption capacity with a critical silt + clay content of 45%. The pH was found to have an indirect effect on phosphate adsorption. The pH coupled with the redox condition determined the free iron content which in turn affected the phosphate adsorption. Organic matter could be a factor in controlling solubilities of iron oxides by affecting the redox potential of the soil environment. It is suggested that the adsorption capacity of soils may be estimated by simple measurements of pH, pe and silt + clay %.

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## SUMMARY

An attempt was made to relate phosphate adsorption capacities, quantified by the adsorption parameters, estimated from Freundlich and Langmuir equations, to other soil properties. The adsorption parameters used are the Freundlich adsorption coefficient (F-a) and the Maximum Buffer Capacity (MBC). From simple correlation analysis, the level of free iron oxides and organic matter and the size of the silt + clay fraction were found to be significantly related to P-adsorption. Partial correlation analysis indicated that pH and silt + clay % played the most important role in P-adsorption. The soils under study may be divided into two groups of P-adsorption capacity depending on the silt + clay content being lower or greater than the critical value of 45%. On further examination of the effect of pH it was found that the interplay of redox potential and pH, determined the formation of free iron oxide in soils. Free iron oxide in turn dictated the process of phosphate adsorption. Equations relating the two adsorption parameters to pH, pe + pH and silt + clay % of a soil were formulated. A simple method of estimating P-adsorption capacity was suggested.

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