

## CHAPTER III



### RESULTS AND DISCUSSION

From the equilibrium time study of three red soils presented in Table 2.5, it seems that the equilibrium time depends on the types of soils and anions concerned. Chloride is the most easily adsorbed by soils whereas sulphate is more difficult and phosphate is the most difficult one. The adsorption pattern is relevant to the type of adsorption, viz, chloride is non-specific but sulphate and phosphate are specific adsorption. The Tha Mai soil adsorbed anions more quickly than the Pak Chong and the Chok Chai soils may be because it has high amounts of free iron oxides (9, 24).

#### 3.1 Chloride Adsorption Studies.

The quantities of chloride adsorbed from HCl solutions by these soils as shown in Table 3.1 confirmed the studies of others (3) that the adsorption is concentration and pH-dependent. The mentioned Table shows that at low pH and high solution concentration, adsorption of chloride are 2.34, 2.85 and 4.11 meq/100g soil for the Chok Chai, the Pak Chong and the Tha Mai soils respectively. The outcome of a number of experiments in which KCl, as well as mixtures of HCl and KCl reacted with these soils are summarized in Table 3.2 and Figs. 3.1-3.3. These Figures show the curves of  $\text{Cl}^-$  adsorbed plotted against the final  $\text{Cl}^-$  concentration in equilibrium solutions from which it can be seen that

- 1) The amount of  $\text{Cl}^-$  adsorbed increases as the pH decreases. The characteristics of the curve is a steep curve at the beginning and shows a nearly linear adsorption of small slope at the end.

Table 3.1 Chloride Adsorption on Three Red Soils from Hydrochloric Acid Solutions.

HCl added	The Chok Chai Soil			The Pak Chong Soil			The Tha Mai Soil		
	pH	Cl <sup>-</sup> in solution	Cl <sup>-</sup> adsorbed	pH	Cl <sup>-</sup> in solution	Cl <sup>-</sup> adsorbed	pH	Cl <sup>-</sup> in solution	Cl <sup>-</sup> adsorbed
meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil
1.89	3.40	2.78	0.51	3.70	2.78	0.51	4.20	2.27	0.76
3.66	2.85	5.56	0.88	3.02	5.30	1.01	3.75	4.29	1.52
4.80	2.65	7.32	1.14	2.83	7.07	1.26	3.70	6.06	1.77
6.69	2.40	10.35	1.52	2.60	9.85	1.77	3.51	8.84	2.27
9.47	2.20	15.40	1.77	2.30	14.90	2.02	3.30	13.89	2.53
11.36	2.10	18.94	1.89	2.20	18.18	2.27	3.14	16.92	2.90
14.27	1.95	24.24	2.15	2.05	23.48	2.53	2.90	21.46	3.54
18.87	1.80	33.08	2.34	1.90	32.07	2.85	2.55	29.54	4.11

Table 3.2 Chloride Adsorption on three Red Soils from Hydrochloric Acid - Potassium Chloride Mixtures.

Cl <sup>-</sup> added		The Chok Chai Soil			The Pak Chong Soil			The Tha Mai Soil		
HCl	KCl	pH	Cl <sup>-</sup> in solution	Cl <sup>-</sup> adsorbed	pH	Cl <sup>-</sup> in solution	Cl <sup>-</sup> adsorbed	pH	Cl <sup>-</sup> in solution	Cl <sup>-</sup> adsorbed
meq/100g soil	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil
0	4.17	4.35	7.07	0.63	4.18	6.82	0.76	4.50	6.06	1.14
0	5.93	4.05	10.86	0.51	4.10	10.35	0.76	4.55	9.34	1.26
0	7.95	4.00	14.39	0.76	4.20	13.89	1.01	4.48	12.88	1.52
0	9.97	4.05	18.58	0.68	4.00	17.93	1.01	4.30	16.92	1.52
0	12.00	3.95	22.22	0.89	4.15	21.46	1.26	4.35	20.45	1.77
4.80	4.04	2.68	14.65	1.52	2.88	14.39	1.64	3.60	12.88	2.40
4.80	5.93	2.70	18.43	1.52	2.90	17.93	1.77	3.60	16.67	2.40
4.80	7.95	2.68	22.47	1.52	2.85	21.97	1.77	3.70	20.45	2.53
4.80	9.85	2.70	26.01	1.64	2.90	25.50	1.89	3.70	24.14	2.59
4.80	12.00	2.70	30.05	1.77	2.90	29.29	2.15	3.75	27.78	2.90
9.47	3.91	2.21	22.98	1.89	2.31	22.47	2.15	3.25	21.21	2.78
9.47	6.19	2.20	27.02	2.15	2.30	26.51	2.40	3.30	25.00	3.16
9.47	8.08	2.20	30.81	2.15	2.32	30.05	2.53	3.28	28.53	3.28
9.47	9.97	2.25	34.59	2.15	2.35	34.09	2.40	3.30	32.57	3.16
9.47	11.87	2.20	38.63	2.02	2.35	38.13	2.27	3.35	36.23	3.22

2) When different concentrations of KCl solution is added, chloride adsorption increases with KCl concentration to an apparent maximum. But adsorption of chloride from HCl-KCl mixture is determined mainly by the amount of HCl added.

3) The magnitude of  $\text{Cl}^-$  adsorbed on these soils is in the following order :- the Tha Mai > the Pak Chong > the Chok Chai. From the analysis of soils, it appears that the amount of  $\text{Cl}^-$  adsorbed on the surface of soils depends so much on the amounts of  $\text{Fe}_2\text{O}_3$  in soils and may be weathering stages. From Table 3.7 the chloride adsorption seems to increase with the increasing amounts of  $\text{Fe}_2\text{O}_3$ .

According to the results of Gebhardt and Coleman (3), which agreed with the reaction mechanism proposed by Hingston et al. (18), they referred to the reversible pH-dependent uptake of  $\text{Cl}^-$  by goethite and other oxide minerals as "non-specific adsorption". Positive sites for non-specific adsorption of  $\text{Cl}^-$  are thought to be created through the acceptance of protons by octahedrally coordinated  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . Proton acceptors in the Oxisol and the Ultisol from the Chok Chai, the Pak Chong, and the Tha Mai soils may be considered to be only free iron oxides because the amount of soluble Al was not found to show any relationships with the adsorption pattern (Table 3.7). These soils have lower chloride adsorption than soils of allophanic type, confirming the findings of Cloos et al. (42) who suggested that allophane consists of a silica-alumina core coated with  $\text{Al}(\text{OH})_3$ . Such a substance would exhibit high chloride adsorption properties.

Since chloride is considered non-specifically adsorbed on soils, the adsorption will depend on the net electrical charge of soil colloids. Makaru and Uehara (2) determined the net charge of colloids with constant

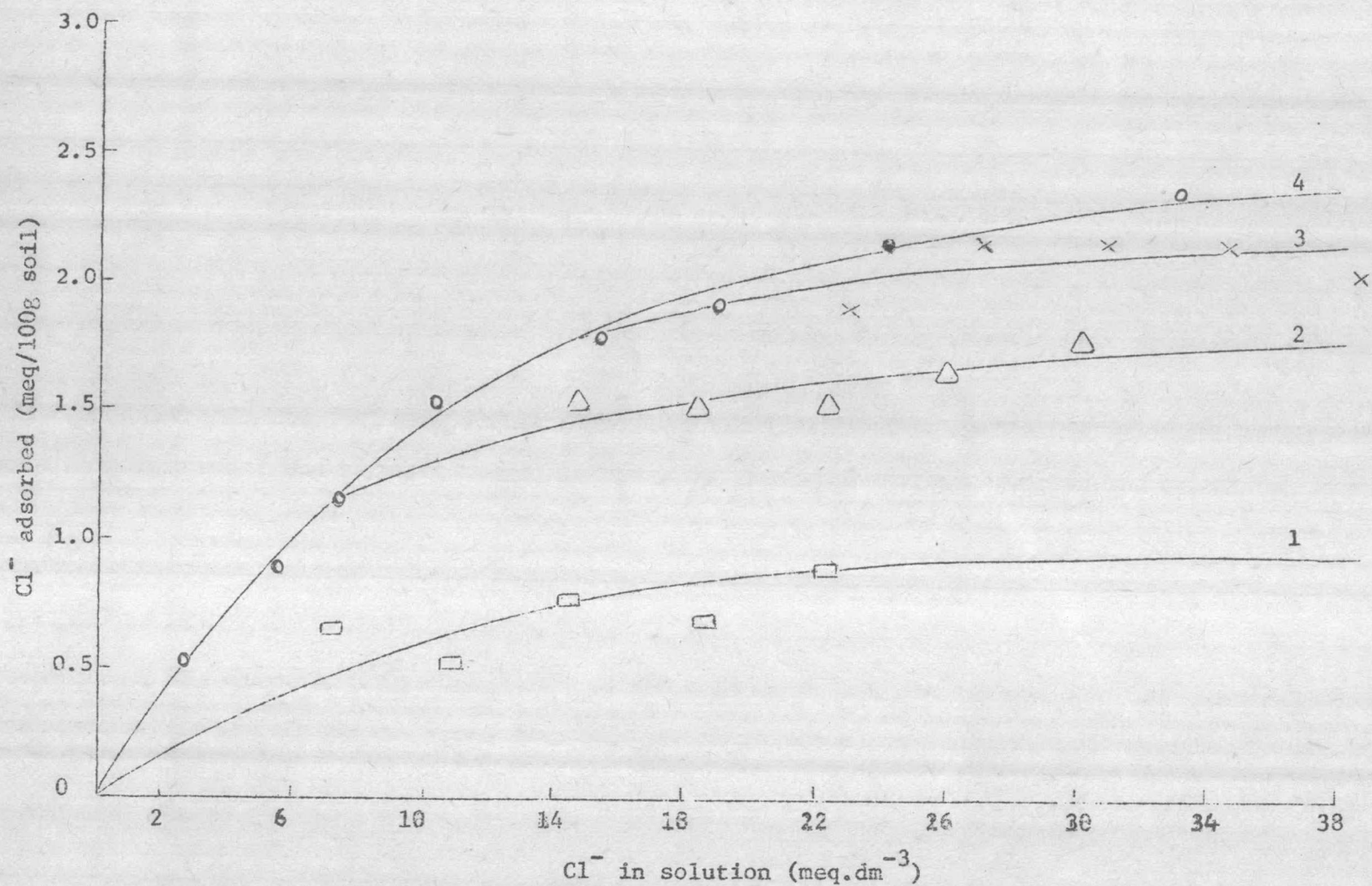


Figure 3.1 Adsorption of Chloride by the Chok Chai Soil. Chloride was added as follows:

- (1) KCl, pH = 3.95-4.35; (2) 4.80 meq HCl/100g + KCl, pH = 2.68-2.70 ;  
 (3) 9.47 meq HCl/100g + KCl, pH = 2.20-2.25 ; (4) HCl, pH= 1.80-3.40 .

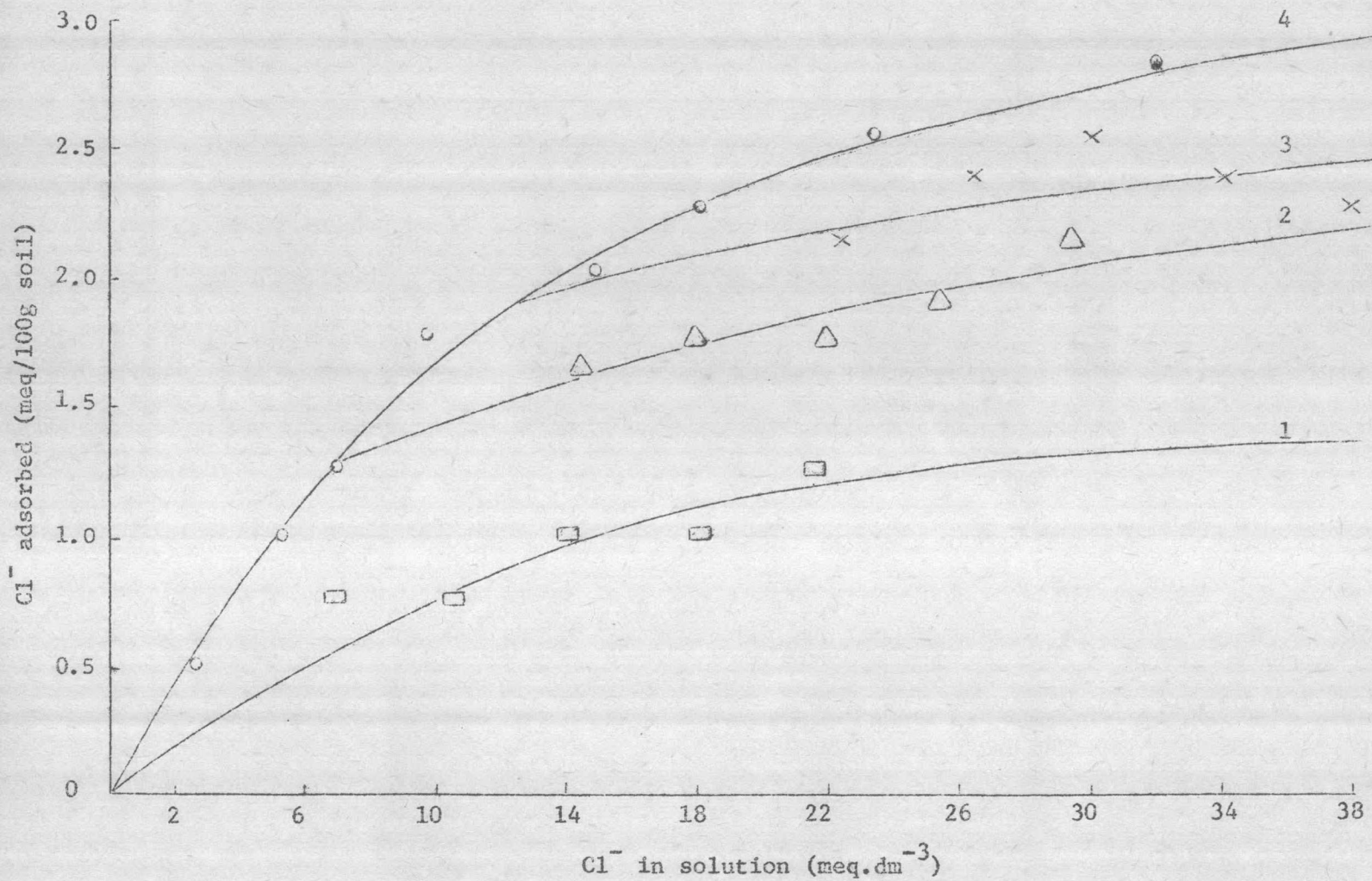


Figure 3.2 Adsorption of Chloride by the Pak Chong Soil. Chloride was added as follows:

- (1) KCl, pH = 4.0-4.2 ; (2) 4.80 meq HCl/100g + KCl, pH = 2.85-2.90 ;  
 (3) 9.47 meq HCl/100g + KCl, pH = 2.30-2.35 ; (4) HCl, pH = 1.90-3.70 .

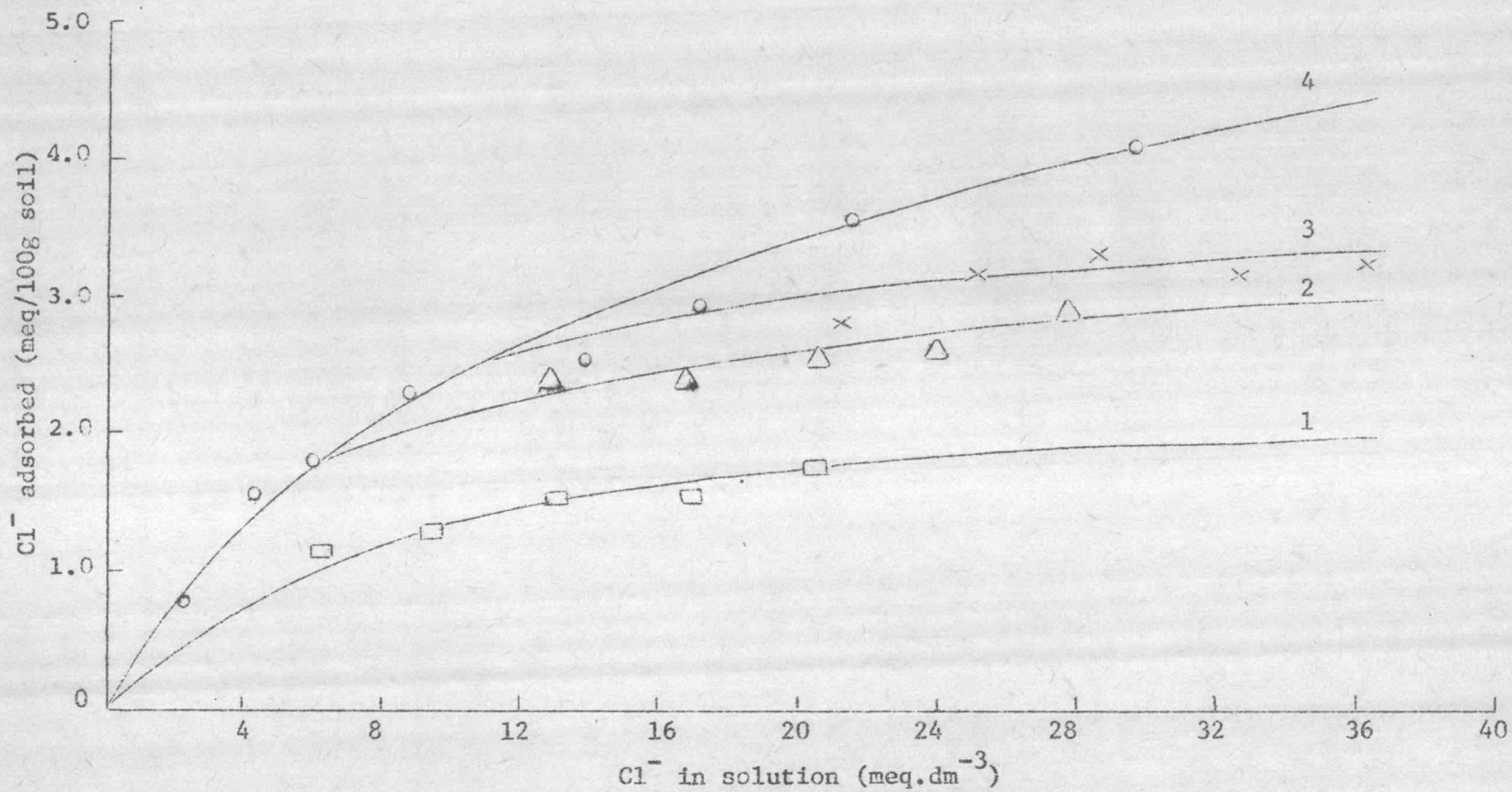


Figure 3.3 Adsorption of Chloride by the Tha Mai Soil. Chloride was added as follows:

- (1) KCl, pH = 4.30-4.55 ; (2) 4.80 meq HCl/100g + KCl, pH = 3.60-3.75 ;  
 (3) 9.47 meq HCl/100g + KCl, pH = 3.25-3.35 ; (4) HCl, pH = 2.55-4.20 .

potential type surface by using the difference in pH of a soil suspension prepared in 1 mol.dm<sup>-3</sup> KCl and water. The quantity (pH KCl-pH H<sub>2</sub>O) called delta pH had a positive, zero and negative values corresponding to the net surface charge. Schofield and Samson (25, 43) showed that kaolinite under acid conditions took up Cl<sup>-</sup> from solution indicating the positive adsorption of Cl<sup>-</sup> exceed negative adsorption. As alkalinity increased, positive adsorption decreased until at high pH values, only negative adsorption occurred. All of the soils used have the net negative charge surfaces, the Tha Mai soil can adsorb more chloride than the Pak Chong and the Chok Chai soils. The Tha Mai soil appears to have the highest negative charge surface, but the highest adsorption occurred is believed to be caused by the effect of the amounts of Fe<sub>2</sub>O<sub>3</sub> on adsorption which is the dominant factor exceeding the effect of net electrical charge on soils.

Chloride adsorption has been used to determine the size and the magnitude of electrical charges carried by clay and oxide mineral (44, 45). Summer and Reeve (45) showed that on the removal of iron oxides, a pattern of adsorption was similar to Schofield and Samson (25, 43) with a smaller positive adsorption at any given pH value. So the presence of small amounts of iron oxides gave rise to large errors in the measurement of edge-charge on kaolinite.

### 3.2 Sulphate Adsorption Studies

The amounts of sulphate adsorbed by three red soils are also strongly dependent upon pH and to a smaller degree upon solution concentration. The amounts of adsorbed SO<sub>4</sub><sup>2-</sup> from H<sub>2</sub>SO<sub>4</sub> solutions by these soils are shown in Table 3.3, adsorption maxima of the Chok Chai, the Pak Chong, and the Tha Mai soils, at low pH and high concentration, occurred at 5.21, 5.52 and 11.24



meq/100g soil, respectively. The adsorption of  $\text{SO}_4^{2-}$  from  $\text{K}_2\text{SO}_4$ , as well as from mixtures of  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  on these soils are summarized numerically in Table 3.4 and diagrammatically in Figs. 3.4-3.6. Interpretation of results is presented below.

1) The amount of  $\text{SO}_4^{2-}$  adsorbed increases as the pH decreases. At the beginning, a steep curve is obtained because the adsorption is high, when more  $\text{H}_2\text{SO}_4$  is added the percentage adsorbed becomes smaller hence a slight curve results.

2) Adsorption increases slowly with the addition of different concentrations of  $\text{K}_2\text{SO}_4$  solutions. Adsorption of  $\text{SO}_4^{2-}$  from  $\text{H}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  mixtures is determined, mainly, by the amount of  $\text{H}_2\text{SO}_4$  added. Adding  $\text{K}_2\text{SO}_4$  to soil-acid mixture resulted in only slightly increasing in adsorption.

3) The magnitude of  $\text{SO}_4^{2-}$  adsorbed on three red soils is in the following order :- the Tha Mai  $\gg$  the Pak Chong  $>$  the Chok Chai soils. Chao et al. (46) showed that the additions of Al and Fe coatings to less retentive soil resulted in considerable increase in sulphate adsorption at all equilibrium pH levels. The magnitude of pH-dependent sulphate adsorption was greater with increasing amount of Fe or Al coating. According to the above workers, no sulphate was adsorbed by soil containing no exchangeable Al or Fe.

Adams et al. (47) showed that the pH-dependent surface charge of Al and Fe oxides, which provided for some kind of  $\text{OH}^- - \text{SO}_4^{2-}$  exchange, was commonly considered to be the mechanism by which sulphate solutions become part of the solid phase. As pH increases, the surface charge becomes less positive, thereby lowering the adsorptive capacity of the oxides for sulphate ions.

Table 3.3 Sulphate Adsorption on Three Red Soils from Sulphuric Acid Solutions.

H <sub>2</sub> SO <sub>4</sub> added	The Chok Chai Soil			The Pak Chong Soil			The Tha Mai Soil		
	pH	SO <sub>4</sub> <sup>2-</sup> in solution	SO <sub>4</sub> <sup>2-</sup> adsorbed	pH	SO <sub>4</sub> <sup>2-</sup> in solution	SO <sub>4</sub> <sup>2-</sup> adsorbed	pH	SO <sub>4</sub> <sup>2-</sup> in solution	SO <sub>4</sub> <sup>2-</sup> adsorbed
meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil
1.64	4.05	0.46	1.41	4.38	0.36	1.46	4.90	0.10	1.58
3.53	3.55	2.20	2.43	3.80	1.53	2.76	4.35	0.56	3.24
4.47	3.40	3.06	2.94	3.65	2.55	3.19	4.30	0.87	4.04
6.34	3.10	6.07	3.30	3.38	4.59	4.04	4.00	1.84	5.42
8.48	2.85	8.98	3.98	3.10	8.68	4.14	-	-	-
9.50	2.70	11.64	3.68	-	-	-	-	-	-
9.71	-	-	-	-	-	-	3.60	4.03	7.69
12.88	2.50	13.07	3.83	2.70	16.03	4.85	3.40	7.45	9.15
16.66	2.35	24.40	4.45	2.45	22.87	5.21	3.22	14.19	9.56
21.46	2.15	32.47	5.21	2.30	31.86	5.52	3.20	20.42	11.24

- = no data

Table 3.4 Sulphate Adsorption on Three Red Soils from Sulphuric Acid - Potassium Sulphate Mixtures.

SO <sub>4</sub> <sup>2-</sup> added		The Chok Chai Soil			The Pak Chong Soil			The Tha Mai Soil		
H <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	pH	SO <sub>4</sub> <sup>2-</sup> in solution	SO <sub>4</sub> <sup>2-</sup> adsorbed	pH	SO <sub>4</sub> <sup>2-</sup> in solution	SO <sub>4</sub> <sup>2-</sup> adsorbed	pH	SO <sub>4</sub> <sup>2-</sup> in solution	SO <sub>4</sub> <sup>2-</sup> adsorbed
meq/100g soil	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil
0	3.96	4.60	4.03	1.94	4.55	3.68	2.12	4.85	2.20	2.86
0	5.75	4.45	7.96	1.76	4.45	7.20	2.15	4.60	4.85	3.32
0	7.51	4.35	10.72	2.15	4.30	10.01	2.50	4.60	6.94	4.04
0	9.50	4.35	14.30	2.35	4.25	12.86	3.07	4.55	9.40	4.80
4.42	3.86	3.45	10.31	3.12	3.60	8.88	3.83	4.30	5.41	5.57
4.42	5.95	3.50	13.89	3.42	3.55	13.48	3.63	4.30	9.19	5.77
4.42	7.84	-	-	-	3.60	16.95	3.78	4.30	12.25	6.13
4.42	8.66	3.50	18.89	3.63	3.50	19.19	3.47	4.25	14.40	6.69
9.77	3.41	2.65	18.68	3.83	2.90	17.36	4.50	3.60	9.39	8.48
9.77	5.66	2.60	21.95	4.45	2.95	21.75	4.55	3.65	12.05	9.40
9.77	8.22	2.65	26.55	4.70	2.90	26.78	4.60	3.55	15.62	10.17
9.77	9.85	2.70	31.14	4.04	2.95	30.20	4.52	3.50	18.58	10.32

- = no data

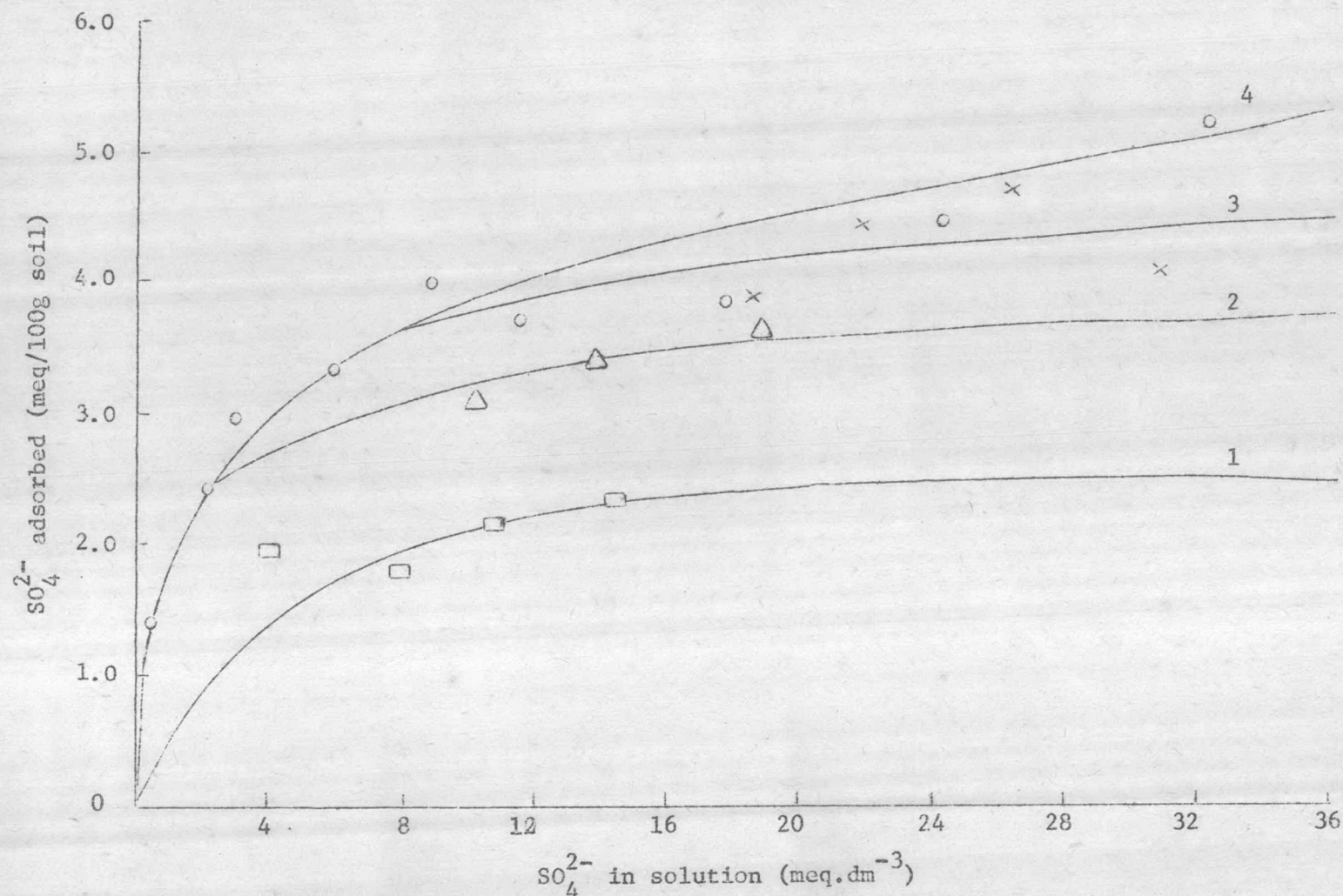


Figure 3.4 Adsorption of Sulphate by the Chok Chai Soil. Sulphate was added as follows:

- (1)  $K_2SO_4$ , pH = 4.35-4.60 ;
- (2) 4.42 meq  $H_2SO_4/100g + K_2SO_4$ , pH = 3.45-3.50 ;
- (3) 9.77 meq  $H_2SO_4/100g + K_2SO_4$ , pH = 2.60-2.70 ;
- (4)  $H_2SO_4$ , pH = 2.15-4.05 .

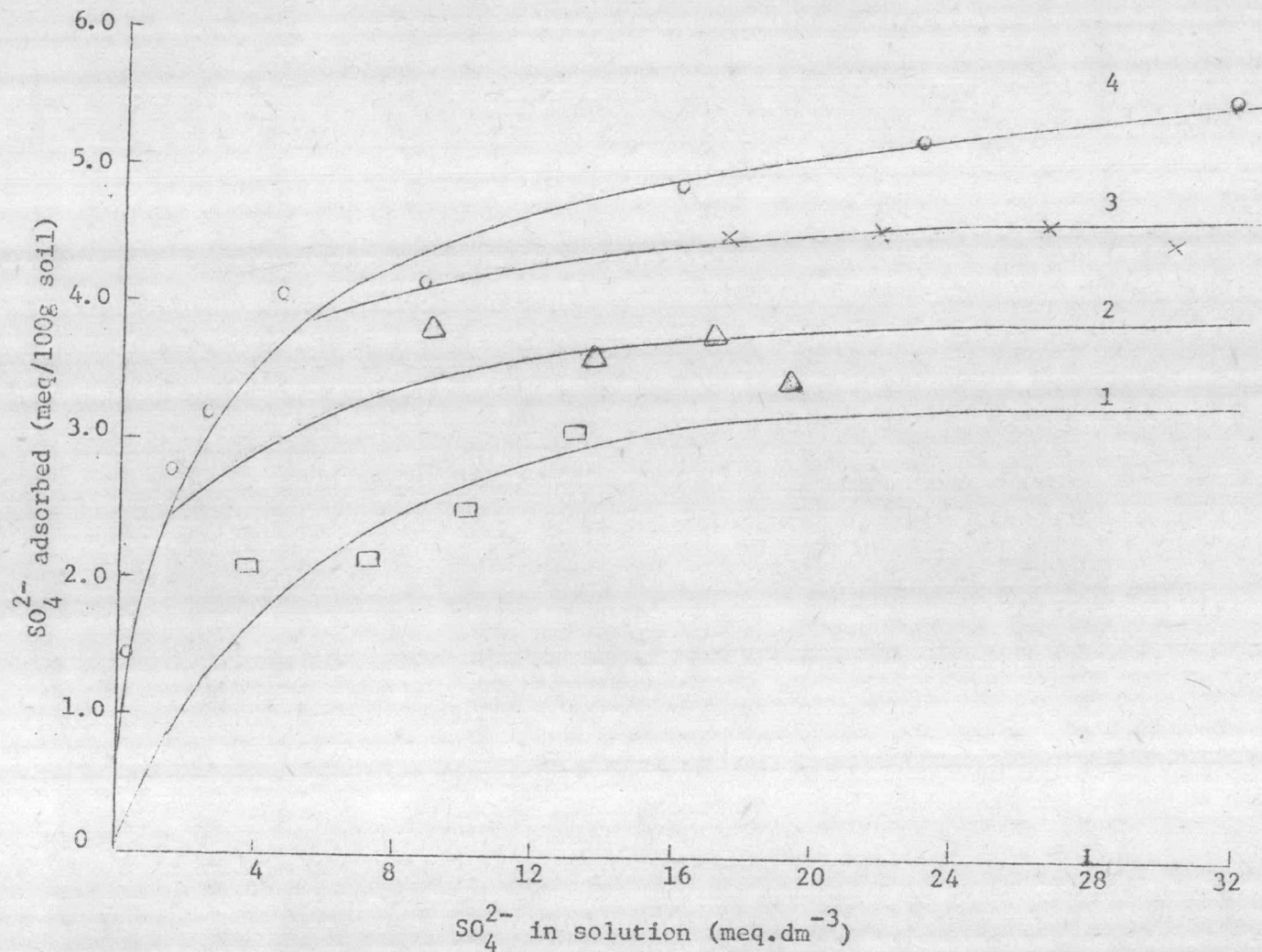


Figure 3.5 Adsorption of Sulphate by the Pak Chong Soil. Sulphate was added as follows:

- (1)  $K_2SO_4$ , pH = 4.25-4.55 ; (2) 4.42 meq  $H_2SO_4/100g + K_2SO_4$ , pH = 3.5-3.6 ;  
 (3) 9.77 meq  $H_2SO_4/100g + K_2SO_4$ , pH = 2.90-2.95 ; (4)  $H_2SO_4$ , pH = 2.30-4.38 .

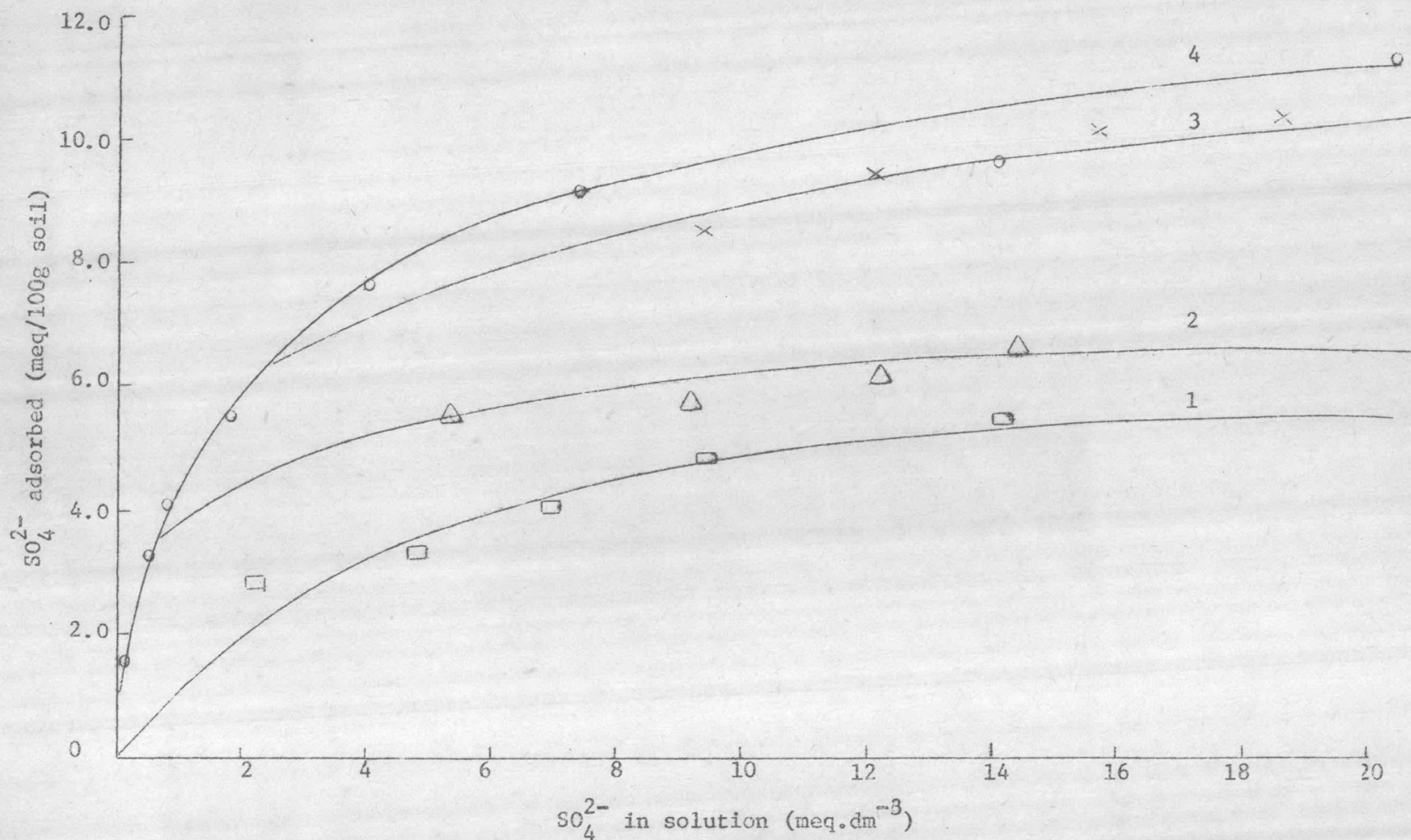


Figure 3.6 Adsorption of Sulphate by the Tha Mai Soil. Sulphate was added as follows:

- (1)  $K_2SO_4$ , pH = 4.55-4.85 ; (2) 4.42 meq  $H_2SO_4/100g + K_2SO_4$ , pH = 4.25-4.30 ;  
 (3) 9.77 meq  $H_2SO_4/100g + K_2SO_4$ , pH = 3.5-3.6 ; (4)  $H_2SO_4$ , pH = 3.20-4.90 .

From the results of Gebhardt and Coleman (4), the number of meq of  $\text{SO}_4^{2-}$  adsorbed per 100g soil was nearly twice the meq of  $\text{Cl}^-$  adsorbed at any pH of each soil. This suggested that the adsorption of sulphate as  $\text{HSO}_4^-$  and that of  $\text{Cl}^-$  used the same reacting site. Barbier and Chabannes (48) reported that  $\text{SO}_4^{2-}$  was retained more strongly than  $\text{Cl}^-$  and Miller (49) showed that increasing the amount of  $\text{Cl}^-$  in the system had no effect on the amount of  $\text{SO}_4^{2-}$  adsorbed. Since the soluble sulphate - sulphur content of the soil samples cannot be extracted by  $0.1 \text{ mol.dm}^{-3}$  HCl solution, it showed that  $\text{Cl}^-$  cannot replace  $\text{SO}_4^{2-}$  because adsorption of  $\text{Cl}^-$  is non-specifically. So the adsorption of sulphate may be specifically adsorbed as proposed by Hingston et al. (13). In the case of sulphate, only the monovalent species,  $\text{HSO}_4^-$ , can be specifically adsorbed without creating any additional negative charge at the surface. The  $\text{pK}_2$  of  $\text{H}_2\text{SO}_4$  is 1.92, and at  $\text{pH} > 4$   $\text{HSO}_4^-$  makes up less than 1 % of the ionic species (4). The adsorption of  $\text{HSO}_4^-$  upon the addition of  $\text{H}_2\text{SO}_4$  to soil would require the rapid protonation of a soil component and the simultaneous adsorption of  $\text{HSO}_4^-$ . The large concentrations of  $\text{K}_2\text{SO}_4$  hardly increase the amount of  $\text{SO}_4^{2-}$  adsorbed in a given narrow range of pH. It shows the significance of  $\text{H}^+$  in the protonation of either a potential adsorption site or a  $\text{SO}_4^{2-}$ . The pH values are so far above  $\text{pK}_2$  that only  $\text{SO}_4^{2-}$  can be adsorbed, with the extent of that reaction severely limited by the development of excess negative charge (4).

Sulphate adsorption and corresponding potassium adsorption when  $\text{K}_2\text{SO}_4$  was added to soils may have proceeded according to the reaction proposed by Chang and Thomas (22) that have already been described. Hydroxyl groups will be replaced by  $\text{SO}_4^{2-}$  and pH value will increase, with the subsequent neutralization of weak-acid exchanged sites. Consequently at a high pH both potassium and sulphate ions are adsorbed. For the low-pH adsorption of

sulphate, it is possible that  $\text{HSO}_4^-$  is adsorbed non-specifically as counterions opposing positively charged sites on oxide surface (4). This is on contrary to Hingston's conclusion (13).

The soils of the Ultisols and Oxisols have lower sulphate adsorption than the soils of Andept because the Andept has large surface areas of Fe-Al oxides, the favorable condition for the sulphate adsorption. From the results of Chao et al. (46) about the addition of Al or Fe coating to the less-retentive soils, they found that sulphate adsorption by Fe-coated soils increased with a decrease in pH without going through a maximum point as observed with Al-coated soils since hydrous Fe-oxide has a lower isoelectric point than hydrous Al-oxide and, hence, was more stable at lower pH values. It is attributed the pH-dependent sulphate adsorption by Thai red soils of the Ultisol and the Oxisol to the presence of hydrous Fe-oxide, or a combination of hydrous Fe- and small amount Al-oxides, but not hydrous Al-oxide alone since no break around pH 4.0 in the pH- $\text{SO}_4^{2-}$  adsorption curve has ever been found in  $\text{SO}_4^{2-}$  - retentive soils. It has been found that Al hydroxide can retain sulphate as much as six times as iron hydroxide at the isoelectric point.

### 3.3 Phosphate Adsorption Studies.

In the case of phosphate, the magnitude of adsorption is very strongly dependent upon pH and solution concentration. The amounts of adsorbed  $\text{PO}_4^{3-}$  from  $\text{H}_3\text{PO}_4$  solution by these soils are shown in Table 3.5, with maxima adsorption at low pH and high concentration, they occurred at 15.71, 15.77 and 20.46 meq/100g soil, of the Chok Chai, the Pak Chong and the Tha Mai soils, respectively. Table 3.6 and Figs. 3.7-3.9 show the relationships between  $\text{PO}_4^{3-}$  adsorbed and  $\text{PO}_4^{3-}$  concentration of solution in the case of  $\text{KH}_2\text{PO}_4$ ,



mixtures of  $H_3PO_4$  and  $KH_2PO_4$  additions to three red soils. The results shown in the mentioned figures are itemised below.

1) Phosphate adsorption increases with decreasing in pH. The slope of the curve is steep at the beginning shows that strong initial adsorption occurred.

2) When different concentrations of  $KH_2PO_4$  solutions was added, phosphate adsorption increases with solution concentration. It shows high affinity adsorption at low solution concentrations and linear increase in adsorption at higher solution concentrations. When the mixtures of  $H_3PO_4$  and  $KH_2PO_4$  are added, the adsorption process has two apparent parts: i) high affinity uptake of  $PO_4^{3-}$  from  $H_3PO_4$  and ii) low affinity uptake of  $PO_4^{3-}$  from  $KH_2PO_4$  (5). These results agree with Parfitts (50) in the experiment on phosphate adsorption of an Oxisol and Gebhardt and Coleman (5) on phosphate adsorption of the allophanic tropical soils.

3) The magnitude of adsorption on these soils is in the following order:- the Tha Mai > the Pak Chong > the Chok Chai soils. The amounts of  $Fe_2O_3$  in these soils appear to have some relationship with the adsorption, since it shows that phosphate adsorption increases with increasing in the amounts of  $Fe_2O_3$  (Table 3.7).

Muljadi, Posner and Quirk (51) have given detailed descriptions of phosphate adsorption by aluminum hydroxide and kaolinite. They regarded  $H_2PO_4^-$  to be the ion adsorbed. Hingston et al. (13) suggested that phosphate, in common with many anions of polybasic acids, was adsorbed specifically on oxide surfaces. Atkinson (52) found that when phosphate was adsorbed by hematite the surface became more negative by ligand exchange of the anion with water molecules or  $OH^-$  coordinated with ferric oxide surface. The similar change in the charge was observed by Hingston et al. (13) for a series

Table 3.5 Phosphate Adsorption on Three Red Soils from Phosphoric Acid Solutions.

$H_3PO_4$ added	The Chok Chai Soil			The Pak Chong Soil			The Tha Mai Soil		
	pH	$PO_4^{3-}$ in solution	$PO_4^{3-}$ adsorbed	pH	$PO_4^{3-}$ in solution	$PO_4^{3-}$ adsorbed	pH	$PO_4^{3-}$ in solution	$PO_4^{3-}$ adsorbed
meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil
2.86	4.71	0.13	2.73	4.80	0.12	2.74	5.40	0.02	2.84
4.25	4.25	0.34	3.91	4.40	0.31	3.94	4.74	0.03	4.22
6.14	4.00	0.67	5.47	4.15	0.53	5.61	4.70	0.05	6.09
8.10	3.75	1.10	7.00	3.95	0.86	7.24	4.50	0.10	8.00
8.90	3.65	1.58	7.32	3.88	1.33	7.57	4.35	0.15	8.75
12.96	3.45	3.08	9.88	3.50	2.43	10.53	4.25	0.29	12.67
17.25	3.25	4.94	12.31	3.38	3.57	13.68	4.05	0.50	16.75
21.31	3.20	5.60	15.71	3.30	5.54	15.77	3.92	0.85	20.46

Table 3.6 Phosphate Adsorption on Three Red Soils from Phosphoric Acid - Potassium Dihydrogen Phosphate Mixtures.

PO <sub>4</sub> <sup>3-</sup> added		The Chok Chai Soil			The Pak Chong Soil			The Tha Mai Soil		
H <sub>3</sub> PO <sub>4</sub>	KH <sub>2</sub> PO <sub>4</sub>	pH	PO <sub>4</sub> <sup>3-</sup> in solution	PO <sub>4</sub> <sup>3-</sup> adsorbed	pH	PO <sub>4</sub> <sup>3-</sup> in solution	PO <sub>4</sub> <sup>3-</sup> adsorbed	pH	PO <sub>4</sub> <sup>3-</sup> in solution	PO <sub>4</sub> <sup>3-</sup> adsorbed
meq/100g soil	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil		meq.dm. <sup>-3</sup>	meq/100g soil
0	1.53	5.08	0.07	1.46	5.65	0.03	1.50	5.80	0.01	1.52
0	3.33	4.70	0.37	2.96	5.55	0.19	3.14	5.60	0.03	3.30
0	5.05	4.60	0.86	4.19	5.23	0.53	4.52	5.00	0.06	4.99
0	7.44	4.64	1.68	5.76	5.12	1.02	6.42	5.45	0.15	7.29
0	9.20	4.70	2.63	6.57	4.90	1.69	7.51	5.35	0.34	8.86
6.75	1.26	4.00	1.26	6.75	4.15	0.88	7.13	4.90	0.13	7.88
6.75	3.17	4.10	2.02	7.90	4.22	1.46	8.46	4.88	0.27	9.65
6.75	5.03	4.02	2.89	8.89	4.28	2.11	9.67	5.05	0.49	11.29
6.75	7.23	4.10	4.20	9.78	4.15	2.97	11.01	4.80	0.84	13.14
6.75	9.86	4.00	4.99	11.62	4.10	3.68	12.93	4.70	1.53	15.08
10.34	0.86	3.81	2.27	8.93	3.95	1.53	9.67	4.85	0.24	10.96
10.34	2.82	3.80	3.12	10.04	4.00	2.32	10.84	4.82	0.45	12.71
10.34	5.01	3.85	4.02	11.33	3.95	3.00	12.35	4.90	0.71	14.64
10.34	7.39	3.88	5.18	12.55	4.02	3.96	13.77	4.75	1.13	16.60
10.34	10.46	3.90	6.31	14.49	3.98	4.65	16.15	5.05	1.70	19.10

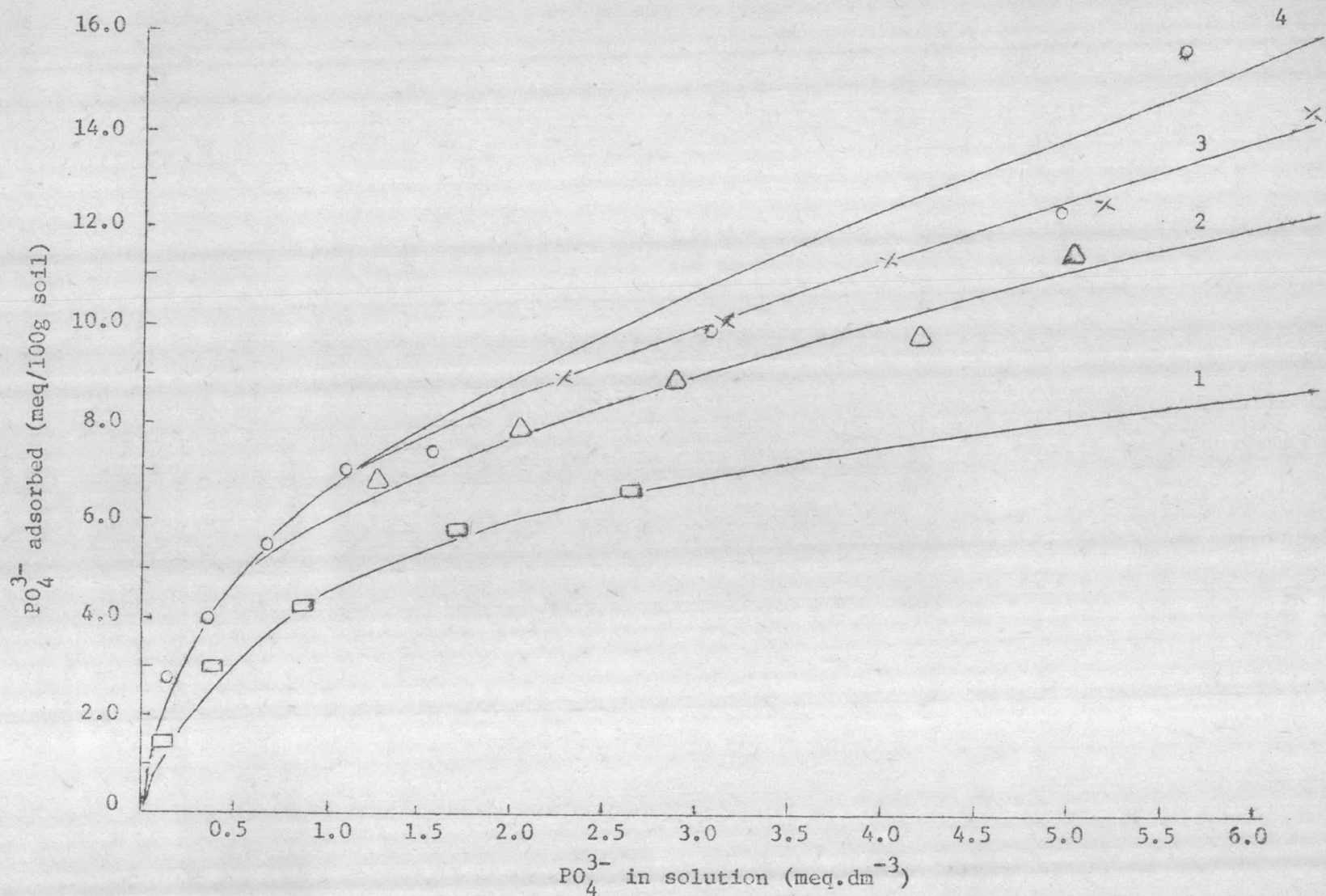


Figure 3.7 Adsorption of Phosphate by the Chok Chai Soil. Phosphate was added as follows:

- (1)  $\text{KH}_2\text{PO}_4$ , pH = 4.60-5.08 ; (2) 6.75 meq  $\text{H}_3\text{PO}_4$ /100g +  $\text{KH}_2\text{PO}_4$ , pH = 4.0-4.1 ;  
 (3) 10.34 meq  $\text{H}_3\text{PO}_4$ /100g +  $\text{KH}_2\text{PO}_4$ , pH = 3.8-3.9 ; (4)  $\text{H}_3\text{PO}_4$ , pH = 3.20-4.71 .

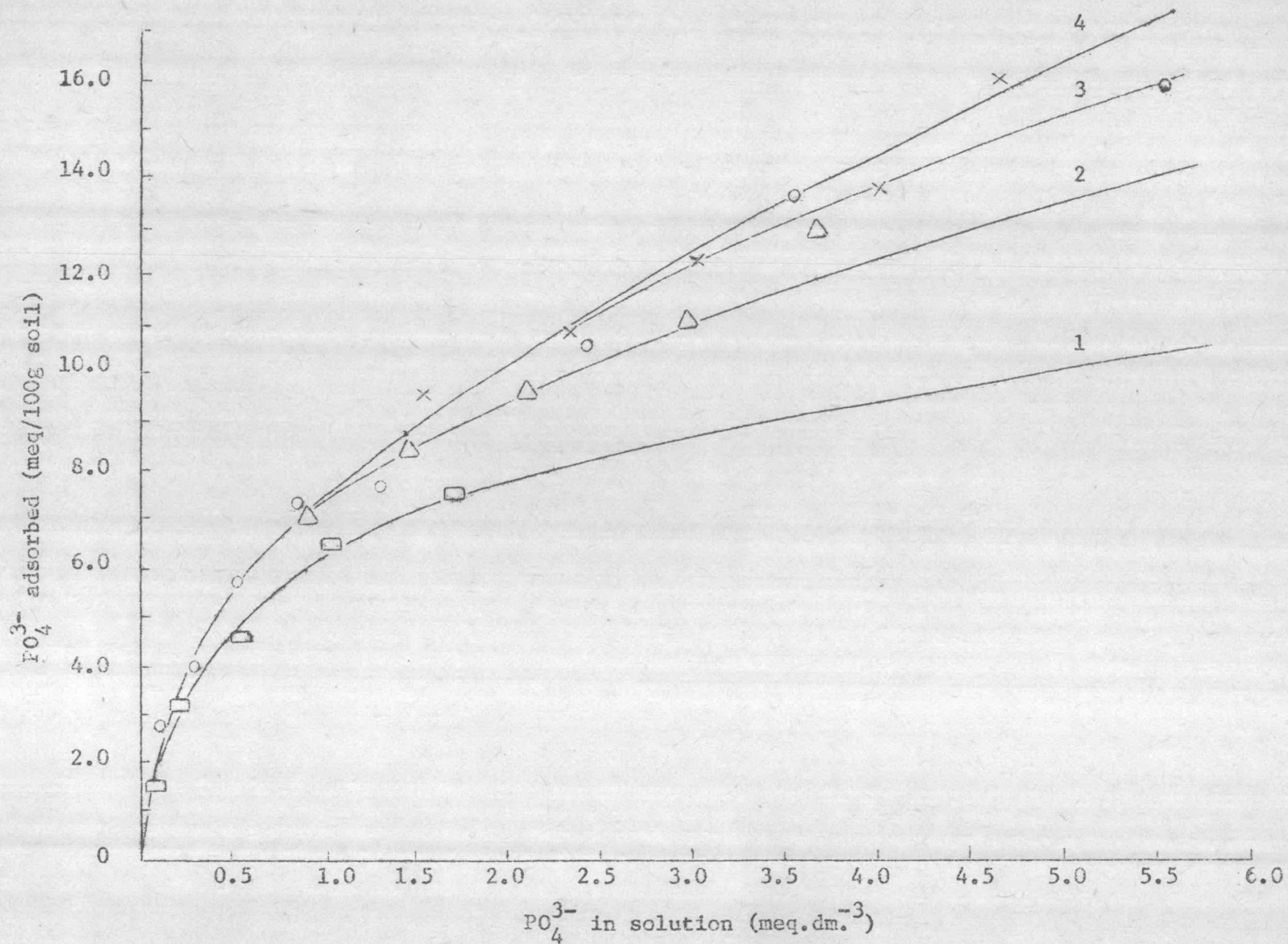


Figure 3.8 Adsorption of Phosphate by the Pak Chong Soil. Phosphate was added as follows:

(1)  $\text{KH}_2\text{PO}_4$ , pH = 4.90-5.65 ; (2) 6.75 meq  $\text{H}_3\text{PO}_4$ /100g +  $\text{KH}_2\text{PO}_4$ , pH = 4.10-4.28 ;

(3) 10.34 meq  $\text{H}_3\text{PO}_4$ /100g +  $\text{KH}_2\text{PO}_4$ , pH = 3.95-4.02 ; (4)  $\text{H}_3\text{PO}_4$ , pH = 3.3-4.8 .

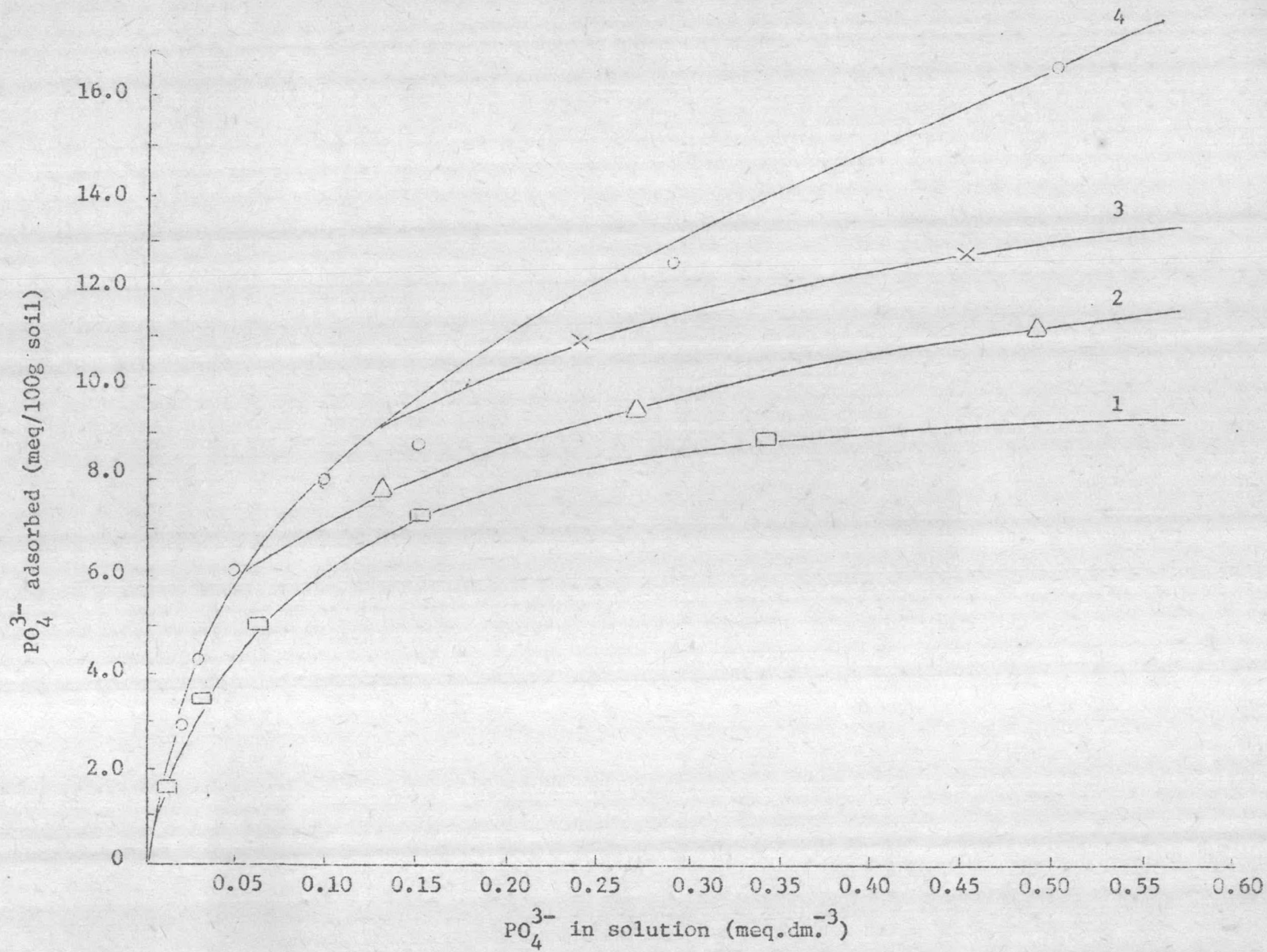


Figure 3.9 Adsorption of Phosphate by the Tha Mai Soil. Phosphate was added as follows:

- (1)  $\text{KH}_2\text{PO}_4$ , pH = 5.35-5.80 ;
- (2) 6.75 meq  $\text{H}_3\text{PO}_4/100\text{g}$  +  $\text{KH}_2\text{PO}_4$ , pH = 4.70-4.90 ;
- (3) 10.34 meq  $\text{H}_3\text{PO}_4/100\text{g}$  +  $\text{KH}_2\text{PO}_4$ , pH = 4.75-5.05 ;
- (4)  $\text{H}_3\text{PO}_4$ , pH = 3.92-5.40 .

of inorganic anions. They concluded that desorption of phosphate could only occur when the displacing anion was specifically adsorbed and present at the sufficient concentration to increase the net negative charge on the oxide surface. Chloride and nitrate ions cannot desorb phosphate because these ions are non-specifically adsorbed and therefore cannot make the surface more negative. But phosphate can be replaced by citrate and hydrogen carbonate ions, however, the concentration of both hydrogen carbonate and citrate ions would be considerably higher in the root zone than in the bulk of the soil solution. Thus plants grow on phosphate deficient soils could make use of hydrogen carbonate ion to desorb phosphate. Plants which produce organic acids could also use the organic anions of these acids in addition to the hydrogen carbonate ion to displace adsorbed phosphate (53). Barbier and Chabannes (48) reported that phosphate was retained more strongly than sulphate and sulphate retention was decreased by the addition of phosphate to the equilibrium solution. So the addition of phosphate to soil will decrease sulphate adsorption and should accelerate the movement of sulphate from the surface to the subsoils.

The results of this experiment appear to agree with Gebhardt and Coleman (5) in which the adsorption increased with decreasing in pH and increasing in solution concentration. Two reactions of adsorption process have been suggested as follows.

1) High-affinity adsorption of  $\text{H}_2\text{PO}_4^-$  on the surface, as reflected by the steep initial portion of the adsorption isotherm. The amount of  $\text{PO}_4^{3-}$  that can be adsorbed in this way apparently depends upon the quantity of protons available for surface protonation and/or combination with displaced hydroxyl.

2) Low-affinity adsorption of  $\text{H}_2\text{PO}_4^-$  and potassium in nearly an equivalent amount, as shown by the gently sloping, giving a nearly linear

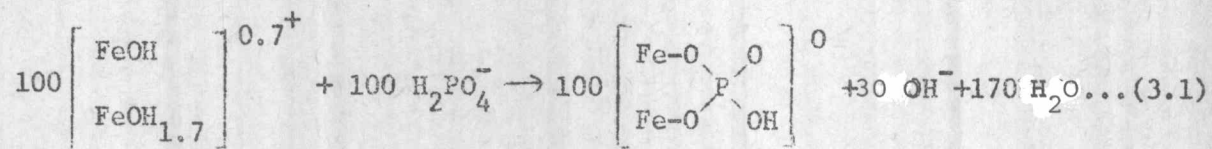
Table 3.7 Some Properties of Three Red Soils that are Related to the Anion Adsorption.

Soil series	Fe <sub>2</sub> O <sub>3</sub>	soluble Al	Δ pH
	Pct.	meq/100g	
The Shok Chai	2.89	1.80	-0.1
The Pak Chong	7.44	4.31	-0.7
The Tha Mai	10.15	0.27	-1.1



portion of the adsorption curves. Lack of protons for surface protonation or reaction with displaced  $\text{OH}^-$  does not prevent further adsorption of  $\text{PO}_4^{3-}$  as the solution concentration of  $\text{H}_2\text{PO}_4^-$  increases, but does require coadsorption of potassium to maintain electroneutrality (13).

Recent work (54, 55) has now firmly established that the adsorption process on synthetic iron oxides is a ligand exchange reaction. It has confirmed Atkinson's hypothesis (56) that phosphate is adsorbed on goethite and other iron oxides by ligand exchange with pairs of Fe-OH to give a bridging binuclear  $\text{FeOP}(\text{O}_2)\text{OFe}$  complex. For example, at pH 5.1 the equation for reaction of  $100 \mu\text{mol.g}^{-1} \text{H}_2\text{PO}_4^-$  with  $200 \mu\text{mol.g}^{-1} \text{FeOH}$  ( $70 \mu\text{mol.g}^{-1}$  being protonated to  $\text{FeOH}_2^+$  at this pH) is as follows (57).



The complex carries a negative charge on the basic side of the point of zero charge (ZPC) and it is protonated at the ZPC, which occurs at pH 5.1 for goethite surfaces half covered with phosphate. Maximum adsorption occurs at low pH, where the surface is positively charged. Adsorption under these conditions is extremely rapid with equilibrium being reached within several hours.

#### 3.4 Anions Adsorption As Related to pH.

Anions adsorption on soil depends on many factors such as the pH of the soil solution, anion species and variety of soil components. Figs. 3.10-3.12 show the relationships between pH of the solutions and adsorptions of chloride, sulphate, and phosphate on three red soils; the Chok Chai, the Pak Chong and the Tha Mai, respectively. The results show that

1) Anions adsorption decreases with increasing in pH. From the analysis of three curves, the curve for phosphate adsorption has a steep slope, indicating that a phosphate adsorption is very strong pH dependent than sulphate and chloride. For sulphate adsorption, however, the adsorption curve of the Tha Mai soil also exhibits a steeper slope than the Chok Chai and the Pak Chong soils, hence it can be concluded that the sulphate adsorption is strongly pH-dependent on the Tha Mai soil.

2) The adsorption affinities on these soils for the three ions studied are markedly different as shown in the following order:  $\text{H}_2\text{PO}_4^- \gg \text{HSO}_4^- \rangle \text{Cl}^-$  at any pH level. It has confirmed the work by Kunin and Meyers (29) which showed the order of increasing adsorption of mineral acids by a hydroxyl form of amberlite to be  $\text{PO}_4^{3-} \rangle \text{SO}_4^{2-} \rangle \text{NO}_3^- \rangle \text{Cl}^-$ .

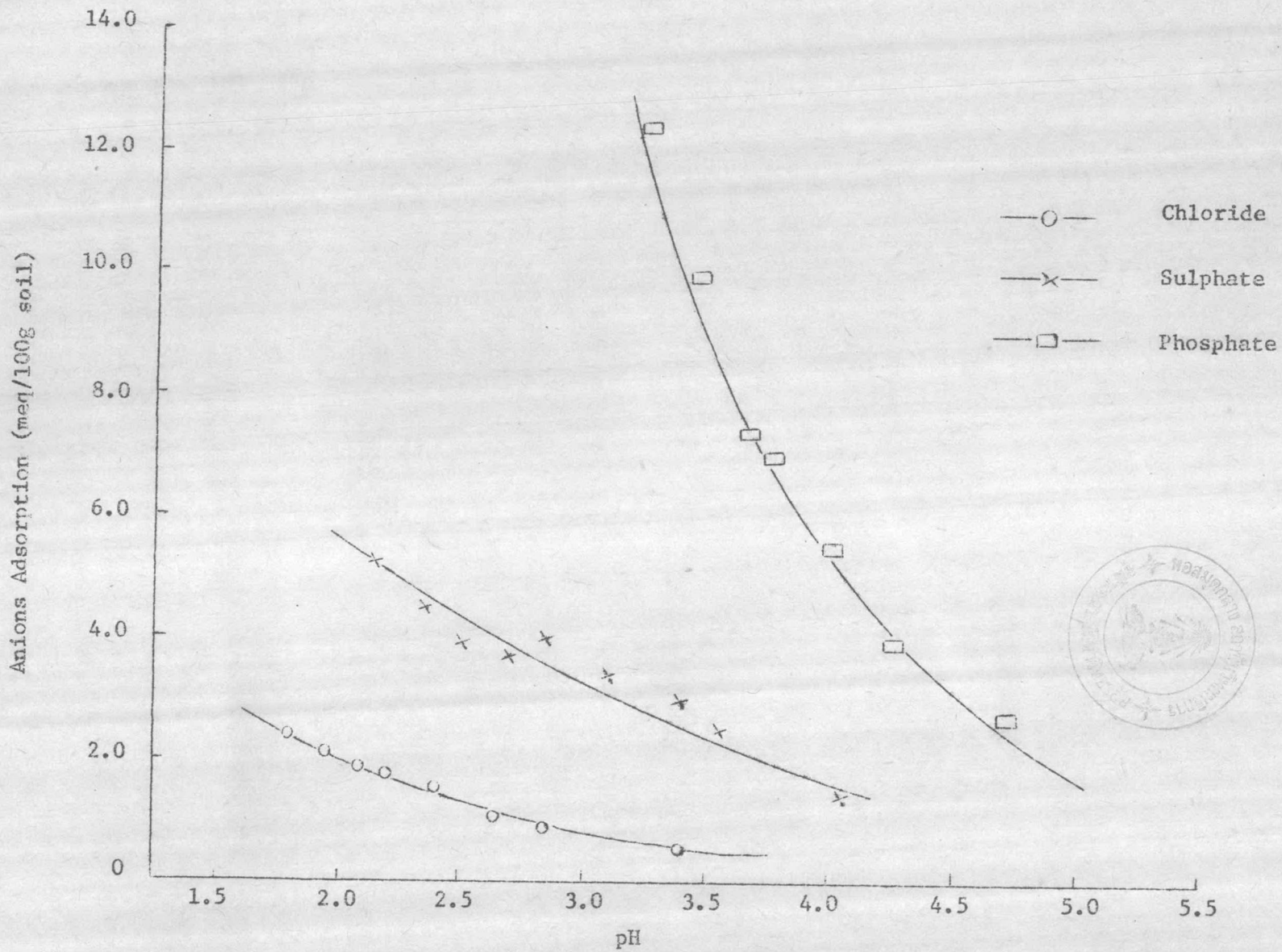


Figure 3.10 Anions Adsorption on the Chok Chai Soil as Related to pH of the Solution

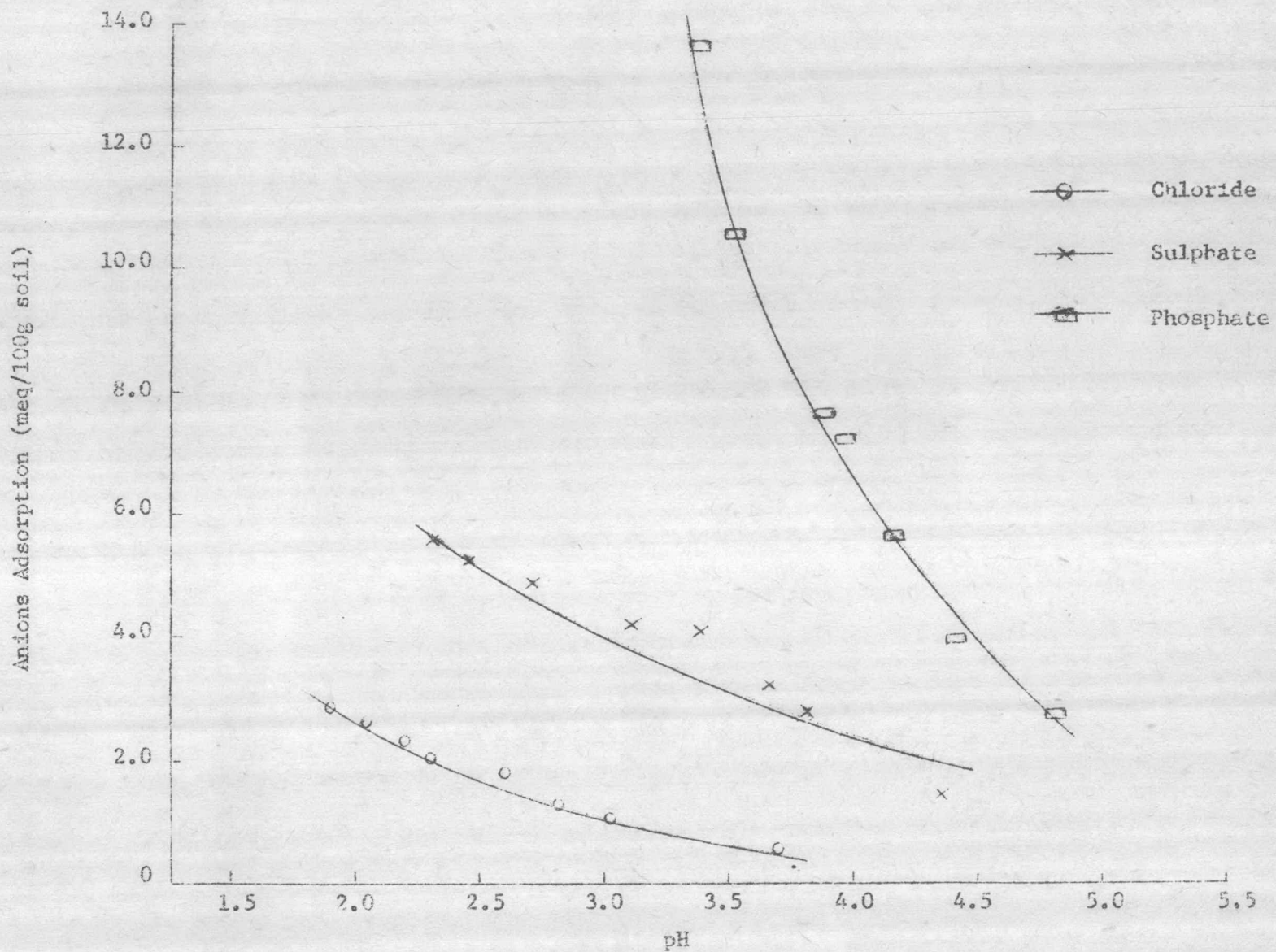


Figure 3.11 Anions Adsorption on the Pak Chong Soil as Related to pH of the Solution.

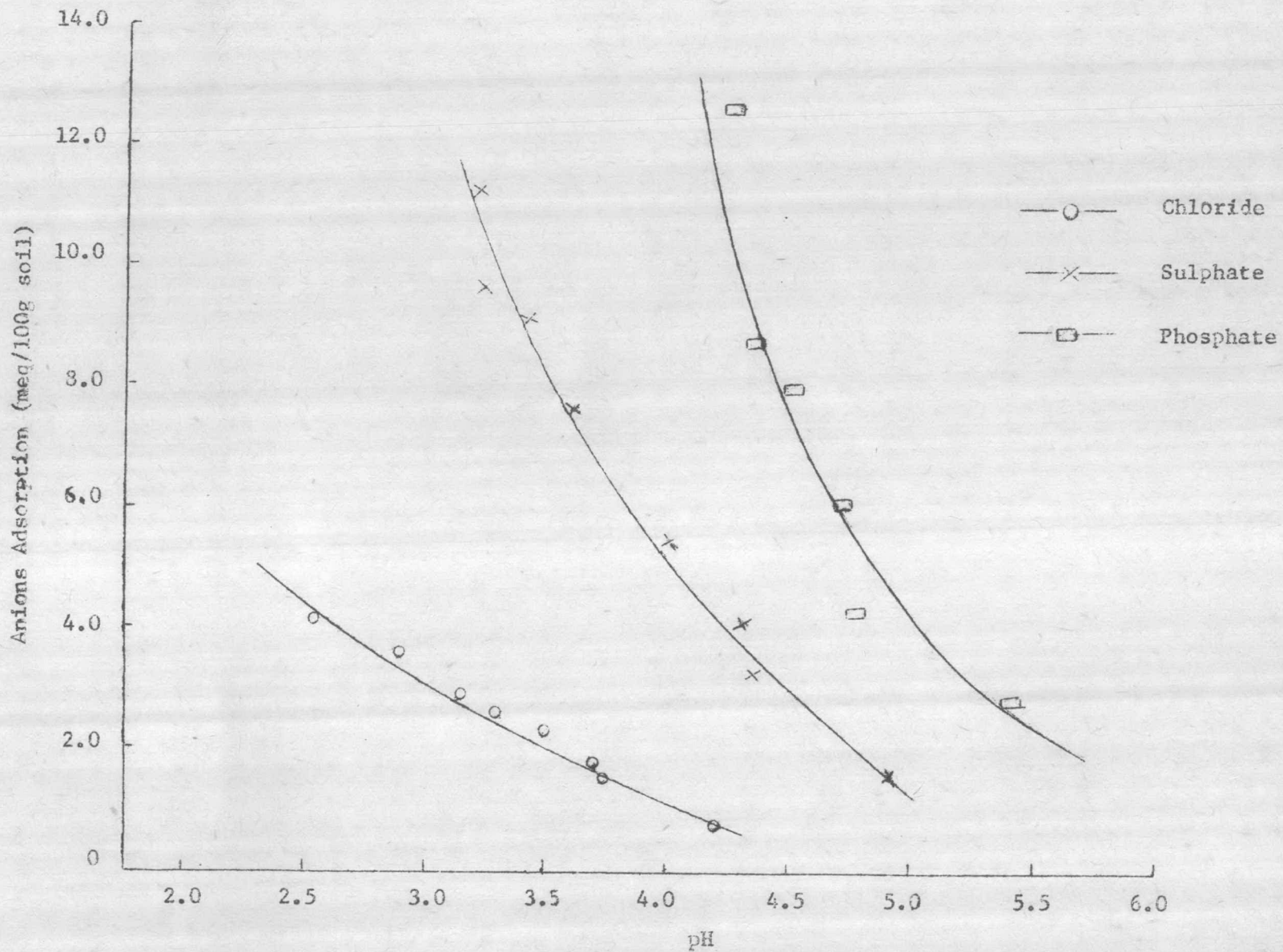


Figure 3.12 Anions Adsorption on the Tha Mai Soil as Related to pH of the Solution.