

EFFECT OF pH ON NI ADSORPTION IN ORGANO-MINERAL COMPLEXES

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Adsorption of nickel on four different soils were studied. These were: Gujranwala series, Kotli series, Lyallpur series and a Pacca series. Effect of organic matter and pH on nickel adsorption were studied. The pH greatly influenced the characteristics of adsorption isotherms. Kotli series H-Clay complexes adsorbed more Ni than corresponding H-clays at all pH while reverse was true in Pacca series, Gujranwala series and mixed behaviour was noted in Lyallpur series. Organic matter solubilization took place at pH >5.0 in Lyallpur series.

Key words: Nickel adsorption, Organic matter, Organo-mineral.

Introduction

During recent years, there has been much interest in the accumulation of heavy metals in soil which are not known to be necessary to plants such as Ni, Pb, Cd etc. The metal pollution of soil in Pakistan is brought about by activities such as sewage sludge waste and pesticide sprays on land. Prolonged use of pesticides containing heavy metals has led to accumulation of Ni, Pb, Cd etc in agricultural soils (Frank *et al* 1976). Environmental hazards derived from heavy metals are strictly linked to their mobility and thus the concentrations of the metals in the soil solution; even if some metals can be complexed with soluble organic matter and may not be available for plant uptake. This is why the distribution of heavy metals between the soil solid phase and soil solution is considered to be of importance in evaluating the environmental consequences of adding materials containing heavy metals to soil (Petruzzelli 1989). Increased Ni concentration in the soil (through sewage sludge applications) are considered to pose potentially serious hazards in the soil-plant-animal system (Cast 1976).

An increase of heavy metals concentration in the soil solution produces a greater plant uptake of the metals, while if they are retained in the soil solid phase as well as organic matter, the environmental hazards can be considered drastically reduced.

Many studies on adsorption of heavy metals by pure clay minerals, soil or organic adsorbents in suspension have shown that pH is a master variable (Alloway 1990). Most of these studies, however, deal with the relationship between the

amount adsorbed and the pH for a given initial amount added to the adsorbent suspension. Since Ni has ionic radius very close to that of Zn, so a similar or very closely related behaviour to Zn may be expected from Ni. The difference between Ni and Zn is that Ni is mostly specifically adsorbed while adsorption of Zn is mostly nonspecific (Harter 1983).

Adsorption of heavy metals on the clay minerals and organic matter is increased by increasing the soil pH (Alloway 1990; Kieke 1984). Presence of organic ligands may increase or decrease Ni adsorption. Zn adsorption increased from pH 3 to 10 with different slopes, and adsorption below pH 5.4 is CEC dependent while above is more pH dependent (Masky and Calvet 1990). Zn adsorption on the clay and hydrous oxides has been shown to be increased (Pickering 1980) or decreased (Kinniberg and Jackson 1982) in the presence of organic ligands.

Use of sewage sludge on agricultural lands is increasing Ni concentration in soils (approaching toxic limits for plants as well as human) and also increasing organic matter contents. Data about effect of organic matter on Ni adsorption in variable charged soils is somewhat available but to our knowledge there is no literature available about permanent charged soils. This experiment was designed to establish direct evidence about effect of organic matter on adsorption of nickel with change in pH in natural clay-humus complexes in permanent charged soils.

Materials and Methods

Four soil samples i.e. Gujranwala series (Hyperthermic Udic Haplustalf), Kotli series (Hyperthermic Chromustert), Lyallpur series (Ustaffic Haplargids) and Pacca series (Ustollic

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Camborhthid) were chosen for study. The parent material of which being alluvium from mixed material from Himalayas. Some description about these soils are given in Table 1. Properties of H-Clays and H-Clay Complexes are given in Table 2.

Extraction of clay-humus complexes ($<2\mu$) from soils. Soil samples were dispersed by sonic vibration and clay fraction ($<2\mu$) was collected according to sedimentation method, dried at $<40^\circ\text{C}$, grinded and passed through 60 mesh sieve. That was natural clay complex. H-clay complexes were prepared by washing with 0.2N HCl until free from calcium ion and then washed with deionized water until free from chloride. Removal of organic matter from H-clay complexes was done by hydrogen peroxide to prepare H-clay.

Clay mineralogy. X-ray diffraction analysis was carried out by using a diffractometer Model No.D/Max 11IC Rigaku Company Japan.

Free iron oxide. Free iron oxide was determined by dithionate-citrate-tartrate bicarbonate (DCB) extractable (Mehra and Jackson 1960).

Adsorption of nickel. One gram of sample was mixed with 20 ml of nickel solution (NiNO_3) in a centrifuge tube. Two drops of chloroform were added to avoid microbial contamination. pH was adjusted to 3, 4, 5, 6, 7, 8, 9, 10 and readjusted after

every shaking. Samples were shaken at room temperature ($24\pm 1^\circ\text{C}$) on reciprocating shaker. After 25 h, suspension was centrifuged, and concentration of nickel in supernatant solution was determined by atomic absorption spectrophotometer (Hitachi A-1800). 10 ppm concentration of nickel was used in all samples except Gujranwala series for which 50 ppm was used.

Results and Discussion

Absorption of nickel influenced by pH for H-clay and H-clay complexes is presented in Fig.1 Nickel absorption increased from pH 3 to 10 with different slopes in all samples except Lyallpur series H-clay complexes. H-clay complexes curves had different slopes than H-clay which signifies that behaviour of organic matter is different from clay minerals. No correlation was found among CEC of soil and amount of adsorption in H-clay as well as H-clay complexes (Table 1 and Fig 1) like northeastern U.S. soils (Harter 1979). Organic matter may be particularly important as a source of pH-dependent retention.

Adsorption increased sharply at >5.0 in H-clay as well as H-clay complexes of Kotli series. This may be due to increase in the number of cation exchange sites on soil of pH-dependent

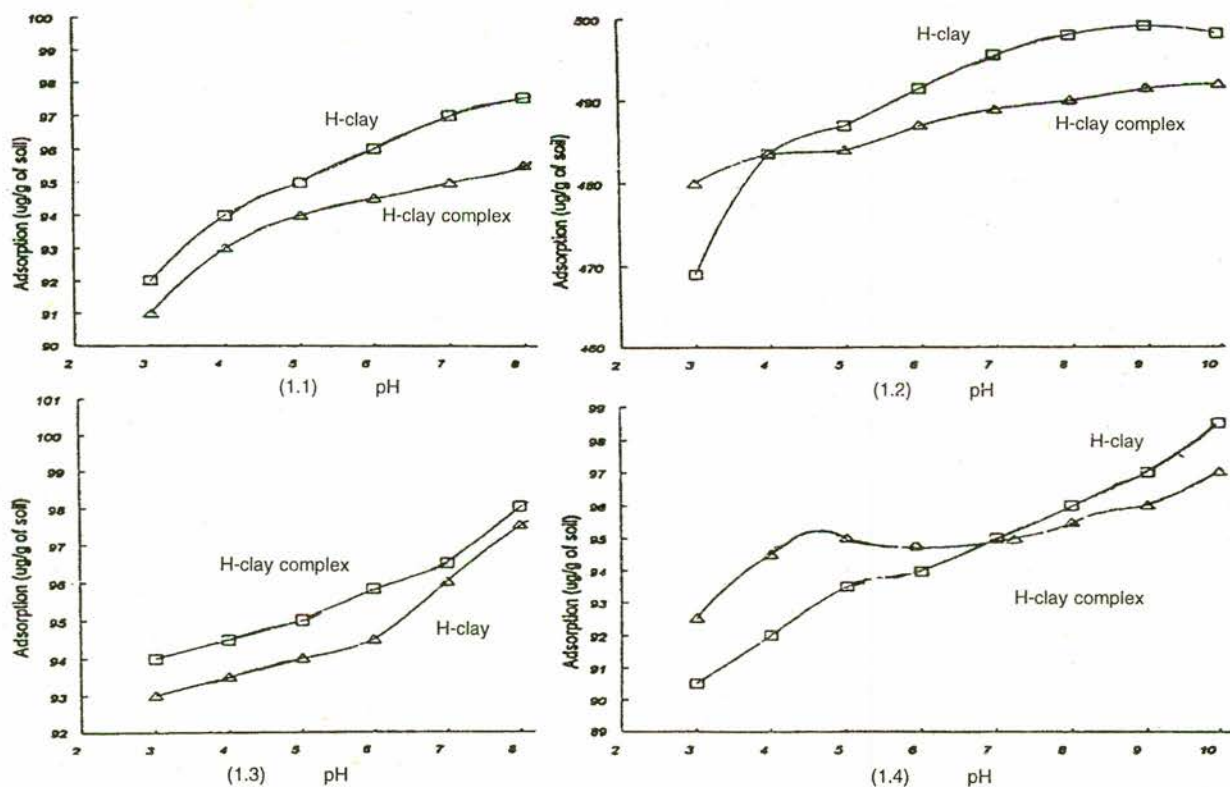


Fig 1. Comparison of H-clays and H-clay complexes, (1.1), Pacca series; (1.2) Gujranwala series; (1.3) Kotli series; (1.4) Lyallpur series.

Table 1
Some properties of soils used

Soil Sample	Depth (cm)	Organic matter (%)	pH in H ₂ O	pH in KCl	CEC m.mol (+kg)	Clay (%)	Free iron oxide (mg ⁻¹ kg)	Amorphous iron oxide (mg ⁻¹ kg)	Crystalline Goethite
Gujranwala Series	0-15	1.84	8.08+	6.96	140.0	18.23#	57.1	70.5	N.D.
Lyallpur Series	0-15	0.79	8.08+	7.15	75.0	16.63#	61.0	28.0	N.D.
Kotli Series	0-15	1.69	7.15+	5.81	300.0	49.33#	89.4	124.0	++
Pacca Series	0-15	1.08	8.47+	7.15	190.0	44.93#	50.5	49.4	N.D.

∨+, Soil Solution ratio (1:1); ++, Small amount detected; ND, Not determined; #, 2μ.

charge surface which may be attributed to Fe-oxide coating on illite, montmorillonite clay mineral and presence of crystalline goethite in this soil (Table 1,2).

The flat curves for H-clays of Pacca series, Lyallpur series and H-clay complexes of Gujranwala series signifies a high buffering capacity whereas steep curves for H-clays of Kotli series, Gujranwala series indicates that the solubility of Ni changes rapidly with change in pH.

Comparison of H-clay and H-clay complexes. Kotli series H-clay complexes adsorbed higher Ni at all pH than respective H-clays. This is in agreement with the results of Italian soils (Petruzzelli *et al* 1992). More adsorption is attributed to increase in negative charge on surface due to organic anions (Parfitt and Russel 1977; Barrow 1985). Pacca series H-clay complexes adsorbed less Ni at all pH than corresponding H-clays, this decrease in adsorption is due to occupation of negative charge (clay minerals surface) by organic matter (Mangaroo *et al* 1965).

Gujranwala series H-clay complexes adsorbed more Ni at pH <4.0, equal at pH 4.0 and less at pH >4.0 than corresponding H-clays. It may be due to high content of free and amorphous iron oxide (Table 1) and high organic matter content (Table 2). Sharp increases in Ni adsorption from pH 3-4 in H-clay may be due to release of Al.

Lyallpur series exhibited mixed behaviour i.e. H-Clay complexes adsorbed more Ni than respective H-Clays at pH <6.0 while reverse behaviour was observed at pH >6.0. This may be due to dissociation of organic matter from the surface (Cavallaro and McBride 1984). It is postulated that functional group begins to dissociate after pH 5.0 and it may be attributed to presence of organic ligands in solution which may decrease Ni adsorption by competing with the surface or for active sites of Ni (Kinniberg and Jackson 1974; Chairidchai and Ritche 1990). At pH >6.0 pH dependent charge is responsible for Ni adsorption but not like Zn (Ansari and Yuan 1994).

Table 2
Some properties of H-clays and H-clay complexes used

Name of soil series	Depth (cm)	pH in H ₂ O	Organic matter %	Clay mineralogy
Gujranwala series	0-15			Ill>Smec>>Kaol, Chl
H-Clay Complex		4.02	2.43	
H-Clay		4.36	0.55	
Kotli series	0-15			Ill>Mont.(Smec)>Kaol, Chl>>Qz
H-Clay Complex		4.39	1.70	
H-Clay		4.43	0.45	
Lyallpur series	0-15			Crys Ill>Smec, Chl>>Kaol, Qz
H-Clay Complex		5.21	2.00	
H-Clay		5.90	0.53	
Pacca series	0-15			Ill>Mont>Chl>>Kaol, Qz
H-Clay Complex		4.55	2.16	
H-Clay		5.44	0.54	

Ill, Illite; Smec, Smectite; Kaol, kaolinite; Chl, Chlorite; Mont, Montmorillonite; Qz, Quartz; Crys Ill, Crystalline Illite.

Conclusion

Organic matter in clay-humus complexes of various origin behaved differently at different pH. It occupied adsorption sites of permanent charged clay mineral surface soils so the decrease in adsorption was caused.

Increase in adsorption of Ni was observed in variable charged surface soil due to organic matter. It was attributed to creation of more negative charge on the surfaces. Organic matter solubilized at pH >5.0 and caused decrease in Ni adsorption at higher pH.

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