Adsorption of nickel by Indian soils

V. Ramachandran[1]*, S.F. D'Souza[1]

[1]*Nuclear Agriculture and Biotechnology Division. Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India.*
*Corresponding author: vrchand@barc.gov.in

Abstract:

Adsorption of metals from liquid into solid phase is one of the most important chemical processes which affect the behaviour and bioavailability of metals in soils, thereby exerts a major influence on their uptake by plant roots. Indian soils, representing the various soil types of tropics, were subjected to Ni treatment of different concentrations and equilibrated at room temperature. The Ni adsorbed by each soil was calculated as the difference between the amount of Ni present in the solution initially and that remaining after equilibration. Results indicated that all the soils under study follow Freundlich and linear adsorption isotherms with highly significant positive correlation. In general, adsorption capacity of the soils for Ni increased with an increase in pH of the soil, whereas, the reverse was found to be true for the rate of adsorption. Significant positive correlations ($p = 0.1 – 0.001$) were obtained between Freundlich's K (adsorption capacity) and pH, CEC and $CaCO_3$ content of the soils. Also, eight soils of Maharashtra, India, were found to fit in all the three adsorption isotherms, namely, Freundlich, Langmuir and linear. The distribution coefficient (K_d) values of these soils, in general, increased with an increase in pH and CEC of the soils. Adsorption of Ni in soils followed the order: vertisol > entisol > alfisol/ultisol.

Keywords: adsorption, nickel, Indian soils, isotherm, distribution coefficient

1. Introduction

Nickel (Ni) is an important heavy metal, and pollution by Ni has gained importance due to the greater understanding of its persistence and toxicity in the ecosystems (Alemayehu and Lennartz, 2010). The effects of Ni exposure vary from skin irritation to damage of the nervous system and it is also a known carcinogen. Nickel may enter and accumulate in agricultural soils through the application of phosphate fertilizers, pesticides and other waste materials from industries like nickel-cadmium batteries, nickel

electroplating, paints formulation, vegetable fat production, etc. The normal range of Ni in soils is 2-750 mg kg^{-1} and the normal range in plants is 0.02 – 5 mg kg^{-1} (Alloway, 1990). The passage of Ni from environment to animals and man involves the transfer of metal through soil-plant link in the terrestrial food chain and hence, the behaviour of Ni in soils and soil-plant system is of considerable environmental significance. The persistence of Ni in the soil and its reduction in mobility involve the phenomena of

sorption, desorption, precipitation, complexation, oxidation/reduction and dissolution. Although all these reactions can occur simultaneously, adsorption mechanisms are known to be determinant in the control of metal availability and solubility in the soil (Sparks, 1999).

Adsorption of metals from the liquid phase into the solid phase is one of the most important chemical processes which affect the behaviour and bioavailability of metals in soils. This process controls the concentration of metal ions and complexes in the soil solution and thus can exert a major influence on their uptake by plant roots.

Adsorption of heavy metals in soils involves two mechanisms. One is non-selective adsorption, in which the metallic cations act as counter-ions in the diffuse layer; the other is selective adsorption, in which surface complexes are formed. The importance of each of these mechanisms depends on the metal and the type of soil (Lafuente *et al*., 2008). Knowledge on the adsorption mechanisms and their quantification are fundamental for the comprehension of polluter-metal movement in contaminated soils, providing possible alternatives for a preventive environment control (Mellis *et al.*, 2004).

The pH, cation exchange capacity and $CaCO_3$ content of the soils are some of the important characteristics which affect the adsorption and subsequent plant uptake of Ni from soil. Soil organic matter exhibits a large number and variety of functional groups and high CEC values, which results in enhanced heavy metal retention ability, mostly by surface complexation, ion exchange and surface precipitation (Bradl, 2004).

Studies on the contamination of Ni in soils and plants have so far been restricted to highly industrialized temperate regions (Reddy and Dunn, 1986; Al-Hamdan and Reddy, 2006) and the quantitative data available on the fate of this pollutant in soils of sub-tropical and tropical regions of Asia, in general, and India, in particular are few.

In the present paper, the adsorption behaviour of Ni by different tropical soils of varying physicochemical characteristics, from different parts of India, was examined using Freundlich, Langmuir and linear adsorption isotherms to understand the likely availability of Ni to agricultural crop plants.

2. Materials and Methods

Soils from 13 places from different parts of India, varying in their physicochemical properties (Table 1) were selected for this study. They broadly represent the four typical soil types of tropics, namely, alfisol, ultisol, entisol and vertisol.

Sieved soils (1 g) of each type were placed in centrifuge tubes at room temperature ($25 \pm 1^{\circ}C$) and 20 mL of 0.01 M $CaCl_2$ containing different concentrations of Ni (ranging from 10 to 100 µg mL^{-1}) were added and shaken for 1 h in a rotary shaker. The soils were then centrifuged at 3000 rpm and filtered through Whatman No. 42 filter paper. The procedure followed here was that of Fontes and Gomes (2003) and there were four replicates for each concentration. The filtrates were analysed for Ni using GBC Model 932B+ atomic absorption spectrometer. The Ni adsorbed by each soil was calculated as the difference between the amount of Ni present in the solution initially and that remaining after equilibrium, as described by Garcia-Miragaya and Page (1978).   The adsorption data of Ni by different soils were examined for the kind of adsorption isotherms they fit, namely, Freundlich, Langmuir or linear adsorption isotherms; their respective equations were as follows:

(i)   Freundlich: $\log x/m = \log K + a \log C$

(ii)   Langmuir: $C/x/m = 1/kb + C/b$

(iii)   Linear: $x/m = a + bC$

Table 1. Physicochemical characteristics of experimental soils

Soil	Soil Group	pH	CEC [c mol (p$^+$)kg^{-1}]	Free CaCO$_3$ (%)	Organic C (%)	Sand (%)	Silt (%)	Clay (%)
Thrissur	Ultisol	4.2	25.9	1.12	3.80	50.8	13.1	36.1
Phondaghat	Ultisol	5.1	10.5	1.00	1.36	59.0	19.0	22.0
Dapoli	Ultisol	5.5	19.3	0.75	0.20	37.0	29.0	34.0
Lanja	Alfisol	5.9	14.6	1.25	1.80	18.0	17.4	64.6
Chittoor	Alfisol	6.4	13.0	0.50	0.12	66.6	20.0	13.4
Mahad	Entisol	6.6	31.6	3.00	1.36	36.8	51.8	11.4
Delhi	Entisol	7.4	18.0	1.55	0.51	73.9	11.2	14.9
Pantnagar	Entisol	7.8	24.4	2.30	1.68	24.0	45.0	31.0
Akola	Vertisol	7.8	51.1	2.60	0.06	21.8	26.0	52.2
Amaravati	Vertisol	8.1	50.0	5.05	0.84	6.5	27.4	66.1
Hatkanangale	Vertisol	8.2	60.7	6.75	1.32	31.4	41.9	26.7
Jalna	Vertisol	8.4	58.1	11.37	0.80	46.0	31.6	22.4
Jalgaon	Vertisol	8.5	40.5	1.60	0.82	28.0	31.0	41.0

where, x/m = Ni adsorbed (µg g^{-1} soil)

C = Ni concentration of equilibrium soil solution (µg mL^{-1})

Freundlich's K = adsorption capacity or degree of affinity (µg Ni g^{-1} soil)

and a = rate of adsorption

Langmuir's k = constant related to bonding energy

b = adsorption maxima (mg Ni g^{-1} soil)

Linear a, b = constants

The Freundlich and Langmuir adsorption parameters were calculated for each soil and the relationships between these parameters and the soil properties such as pH, CEC, organic C, CaCO$_3$ and Clay contents were examined. The distribution coefficient (K$_d$) of Ni for each soil was calculated (Reddy and Dunn, 1986; Anderson and Christensen ,1988; Covelo *et al.*, 2004) using the following formula:

Distribution Coefficient (K$_d$) = Amount of Ni adsorbed g^{-1} soil/Amount of Ni in solution mL^{-1}.

3. Results and Discussion

Results indicate that all the soils under study followed Freundlich and linear adsorption isotherms with highly significant positive correlation (r). Comparatively, the soils followed Freundlich adsorption isotherm better than that of linear adsorption as indicated by higher r values.

The intercepts of linear adsorption equations of different soils, considered as indicators of degree of affinity of the surface for Ni ranged from -109 for Thrissur soil (pH 4.2) to a maximum of 272 for Akola soil (pH 7.8). Echeverria *et al*. (1998) reported that Langmuir monolayer and Freundlich distribution coefficients were higher in basic soils than in acidic soils. A similar trend was observed in the Freundlich adsorption isotherms as indicated by a very small K value (degree of affinity or relative adsorption capacity) of 3.72 for the acidic soil of Thrissur and the highest value of 316.2 for the basic soil of Jalna (Table 2). Typical linear (plot of x/m Vs C) and Freundlich (plot of log x/m Vs C) adsorption isotherms are shown in Figures 1A and 1B, respectively.

The values of Freundlich adsorption parameters 'K' (adsorption capacity) and 'a' (rate of adsorption) are shown in Table 2. In general, adsorption capacity of the soils for Ni increased with an increase in pH of the soil, whereas, the reverse was found to be true for the rate of adsorption. Our findings are in agreement with earlier work of Mellis *et al*. (2004), who also reported that independent of the treatment, the adsorption of Ni increased with increasing pH of the soils.

       The coefficient of correlation of Freundlich adsorption parameters 'K' and 'a' with soil properties are shown in Table 3.

Significant positive correlations (*p* = 0.1 – 0.001) between K and soil properties such as pH, CEC and CaCO$_3$ content were obtained. However, organic C and clay contents did not show any significant correlations. Also, significant negative correlations were obtained between 'a' and pH, CEC of the soils.

Table 2. Values of Freundlich parameters for different experimental soils.

Soil	Adsorption capacity (K) (µg g^{-1} soil)	Rate of adsorption (a)
Thrissur	3.72	1.23
Phondaghat	12.88	0.85
Dapoli	33.90	0.75
Lanja	25.12	0.67
Chittoor	16.22	0.78
Mahad	81.28	0.62
Delhi	64.57	0.68
Pantnagar	125.90	0.55
Akola	309.00	0.58
Amaravati	281.80	0.65
Hatkanangale	295.10	0.65
Jalna	316.20	0.63
Jalgaon	239.90	0.58

Table 3. Coefficient of correlation of Freundlich adsorption parameters with soil properties

Soil property (unit)	K	a
pH	0.946[***]	-0.842[**]
CEC [c mol (p$^+$) kg^{-1}]	0.961[***]	-0.842[**]
Org. C (%)	NS	NS
Clay (%)	NS	NS
CaCO$_3$ (%)	0.659[*]	NS

*: Significant at p = 0.1; **: Significant at p = 0.01 ; ***: Significant at p = 0.001; NS: Not significant
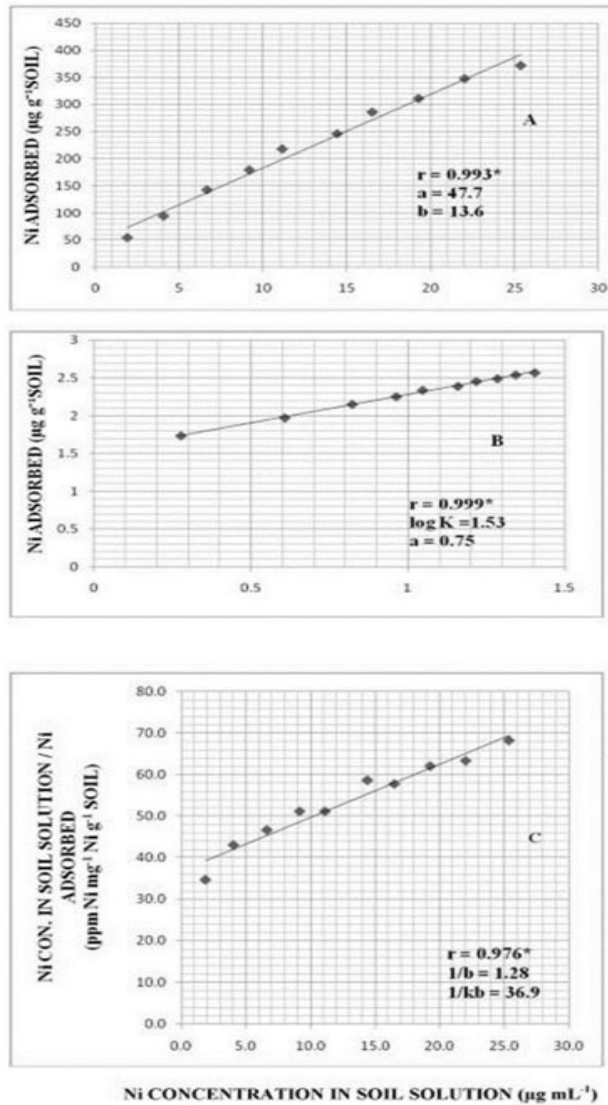
Figure 1. Adsorption of nickel in Dapoli soil A) Linear isotherm B) Freundlich isotherm C) Langmuir isotherm
*: $p = 0.001$.

The current findings are in agreement with earlier studies of Gomes *et al*. (2001) and Adhami *et al*. (2008), who have reported that pH and CEC of soils played major role and were positively correlated with Ni adsorption of soils. According to Adhami *et al*. (2008), adsorption maxima of Langmuir adsorption isotherm of Ni was correlated with CEC of different soils; further, pH, CEC, clay and organic matter contents were the main factors which regulate the retention of Ni in soils. Shi *et al*. (2012) have reported that Ni adsorption on soil organic matter (SOM) was dominant in the short term and the slow transfer of adsorbed Ni to Ni- layered double hydroxide (Ni-LDH) phases with longer reaction times.

Among the 13 experimental soils selected for the study, eight soils of Maharashtra, India, were found to fit in all the three adsorption isotherms, namely, Freundlich, Langmuir and linear and a typical Langmuir adsorption isotherm (plot of C/x/m Vs C) is shown in Figure 1C.

However, in all these eight soils, Freundlich's adsorption isotherm was predominant (r = 0.987 to 0.999) followed by linear (r = 0.974 to 0.993) and least by Langmuir (r = 0.675 to 0.976) as shown in Table 4. The predominance of Freundlich adsorption model for Ni adsorption in soils is in agreement with earlier studies of Al-Hamden and Reddy (2006) and Sunil Kumar *et al.* (2009).

The Freundlich's K values (Table 2) varied from 12.88 for Phondaghat soil of pH 5.1 to 316.20 for Jalna soil of pH 8.4.   Similar trend was followed in Langmuir adsorption isotherm where adsorption maxima (b) values (Table 4) were found to be minimum for Phondaghat soil (0.78) and maximum for Jalna soil (2.63). In general, the adsorption of Ni in different soil types followed the order: vertisol > entisol > alfisol/ultisol.

Earlier researchers have reported about the enhanced sorption of metals with increasing soil pH (Harter, 1983; Msaky and Calvet,1990; Basta and Tabatai, 1992; Raghupathi and Vasuki, 1993), which is attributed to the generation of pH-dependent sites on colloids, reduced competition with H-ions and a change in the hydrolysis state of ions in solution. According to Gomes *et al*. (2001),

soils from alfisol and ultisol orders having higher pH values were the ones with highest relative capacity to adsorb metal ions. Soil with high CEC resulted in greater adsorption of Ni and higher Kd value than the soil having lower CEC.

The findings obtained in the present study are in agreement with Reddy and Dunn (1986), who reported that the abundance of exchange sites available for Ni on high CEC soils were responsible for such observation. Jalali and Moharrami (2007) also have reported that soil with highest CEC showed the highest sorption capacity of the elements studied.

The enhancement in Ni adsorption at higher alkaline pH levels may be attributed to the hydroxide precipitation reactions with Ni^{2+} and $NiOH^+$ species as reported by Sen Gupta and Bhattacharyya (2006). Also, at elevated pH, the presence of carbonates may have led to an increase in the retention of Ni. When the carbonate content and the pH are high, heavy metals are retained in the soil mainly as carbonate salts.

When the pH of the soil decreases, carbonate dissolution increases and ionic exchange is the principal retention mechanism of heavy metals (Plassard *et al.*, 2000; Elzahabi and Yong, 2001).

The distribution coefficient (K_d) values for the eight Maharashtran soils are presented in Table 5.

In general, K_d values increased with an increase in pH and CEC of the different soils. Distribution coefficients characterize the capacity of the soil to retain a solute and the capacity of a solution phase to mobilize it when it is retained (Reddy and Dunn, 1986). High Kd values indicate that the metal (Ni) has been retained by the solid phase through sorption reactions, while low Kd values show that high concentrations of metal remain in solution.

As compared to alkaline soils, the adsorption capacity of Ni in acidic soils is low (Table 2). The findings are similar to that of Cd adsorption in various acidic soils of

Table 4. Langmuir adsorption equation for Ni in different soils of Maharashtra

Soil	pH	Langmuir equation	Correlation coefficient (r)	b
Phondaghat	5.1	C/x/m = 104+1.3C	0.675[*]	0.78
Dapoli	5.5	C/x/m = 36.9+1.28C	0.976[***]	0.78
Mahad	6.6	C/x/m = 6.85+1.07C	0.969[***]	0.93
Akola	7.8	C/x/m = 3.18+0.52C	0.970[***]	1.92
Amaravati	8.1	C/x/m = 3.88+0.39C	0.849[**]	2.56
Hatkanangale	8.2	C/x/m = 3.22+0.43C	0.962[***]	2.33
Jalna	8.4	C/x/m = 3.32+0.38C	0.877[***]	2.63
Jalgaon	8.5	C/x/m = 4.75+0.54C	0.969[***]	1.85

C: Ni concentration of equilibrium soil solution ($\mu g\ ml^{-1}$); x/m: Ni adsorbed ($mg\ g^{-1}$ soil); b: adsorption maxima (mg Ni g^{-1} soil); *: Significant at $p = 0.05$; **: Significant at $p = 0.01$; ***: Significant at $p = 0.001$

India (Ramachandran and D'Souza, 1999). Lafuente *et al.* (2008) reported about the similarity in the adsorption behaviour of Cd and Ni in different soil samples. The presence of Al^{3+} in acidic soils and its competition for exchange sites might have resulted in reduced Ni adsorption in these soils like Cd (Cavallaro and McBride, 1978). According to Tan (2011), at low pH, majority of Ni (II) was adsorbed in the inter layers of Ca-montmorillonite co-ordianted by six water molecules in an octahedron as an outer-sphere complex; on the other hand, at higher pH, inner-sphere surface complexes are formed. Also, the Fe-oxides present in acidic soils may lead to decreased Ni adsorption by blocking access of Ni to exchange sites as reported by Cowan *et al.* (1992) and Zachara *et al.* (1992) for Cd. The acidic soils selected in the present study contained high amount of sesquioxides (Fe_2O_3 + Al_2O_3) of 17% as compared to alkaline soils (below 8%). Hence, the presence of high amounts of Al^{3+} and Fe^{3+} may be responsible for the low adsorption capacity of Ni in these soils.

Table 5. Distribution coefficient (K_d) of nickel for different soils of Maharashtra

Soil	pH	CEC [c mol (p^+)kg^{-1}]	K_d (mL g^{-1})
Phondaghat	5.1	10.5	6.7
Dapoli	5.5	19.3	13.7
Mahad	6.6	31.6	33.3
Akola	7.8	51.1	128
Amaravati	8.1	50.0	185
Hatkanangale	8.2	60.7	188
Jalna	8.4	58.1	212
Jalgaon	8.5	40.5	201

4. Conclusions

The soils selected for the study, in general, fit in Freundlich adsorption isotherm better than either Langmuir or linear adsorption isotherm for Ni adsorption. High pH, alkaline soils favoured high adsorption of Ni, thereby less availability of Ni for plant uptake, whereas, acid soils adsorbed less Ni and more Ni was present as Ni^{2+} in solution, which may lead to more availability of Ni for plant uptake. The study further indicates that Ni adsorption is mainly dependent on pH, CEC and $CaCO_3$ content of the soils. Adsorption of Ni in tropical soils follows the order: vertisol > entisol > alfisol/ultisol.

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