

Article

Removal of nickel from aqueous solution by low-cost clay adsorbents

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Abstract

Laboratory experiments were performed to investigate the effectiveness of natural clay deposits as a potential low cost adsorbent for the removal of nickel (Ni) from wastewater. Two types of natural local clays deposits collected from Al-Mhawes Mountain, Al-Kharg prefecture and Khulais, Jeddah prefecture were examined for their abilities to remove Ni from wastewater. The effects of Ni concentrations, amount of clay added and pH of the solution on Ni adsorption were studied. The mobility of Ni and its specification were examined in a column experiment under graduate levels of clay deposits (0, 3, 6 and 9 %) and increasing Ni concentration (0, 5, and 10 mg L⁻¹) was examined. The Ni adsorption was found to be higher in the Khulais clay due to its relatively higher cation exchange capacity and specific surface area compared to Al-Mahwes clay sample. The maximum Ni adsorption capacity was observed ranges from 0.036 to 0.090 mg g⁻¹. The highest binding energy constant was obtained in case of Khulais clay deposit (1428 L g⁻¹). The adsorption data followed Langmuir and Freundlich isotherms and correlation coefficients (R²) ranged from 0.90 to 0.99. Column studies results showed that 92-99% of the added Ni was retained in the top soil layer (0-5 cm). The results indicated that local natural clay deposits were capable of removing Ni from wastewater at cost-effective and efficient adsorbent materials in Saudi Arabia.

Keywords adsorption; Ni; pH effect; clay deposits; Langmuir and Freundlich models.

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1 Introduction

Heavy metals are one of important pollutants in wastewater, and it has become a public health concern because of its non-biodegradable persistent nature (Manahan, 2000). Many toxic heavy metals have been discharged into the environment as industrial wastes causing serious problem of soil and water pollution (Al-Jilil and Alsewailam, 2009; Sayyed and Sayadi, 2011; Prajapati, 2012). Nickel is a heavy metal whose natural content in the soil can vary from very small proportion, which qualifies as a trace element to excessively high concentration found in soils (Uren, 1992). Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of nickel pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing (Hannachi et al., 2010). Saudi

Arabia is located in an arid region where water resources are limited, shallow and deep underground wells are the main sources for potable water. The problem is aggravated by lack of rainfall; a practical solution of limited water resources is to reuse wastewater for non-domestic purposes. Adsorption of Ni ions by clay has been reported by (Singh and Harris, 2001; Mellis et al., 2004). Numerous processes exist for removing heavy metals, including ion exchange, precipitation, ultrafiltration, and adsorption. Among these methods, adsorption by natural clay is effective and cheap when compared to other methods. The selection of a wastewater treatment method is based on the concentration of dangerous elements and its cost of treatment. Since low cost purificant-adsorbent system is preferred for removal process, substances such as zeolite, particularly clays are commonly used (Bosso and Enzweiler, 2002). Natural clay minerals have been tested as an alternative material for using as synthetic ion exchangers in water purification due to their good filtration qualities, high porosity and large surface area. They are suitable for use in column operations where the adsorbent is frequently exposed to high pressures within system (Baker and Khalili, 2007).

Due to high cost and losses of activated carbon in the application processes, there is growing interest in using low-cost alternative materials including clay, zeolite, coal, fly ash, peat, siderite, agricultural wastes and charcoal. Generally adsorbent can be termed as low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from industry. In Saudi Arabia, large deposit of clay minerals was explored in different locations. The possibility of Saudi Arabian clay as low-cost adsorbent for Ni has been assessed in current research. This study investigated the possibility of two natural clay deposit collected from different places in Saudi Arabia to determine whether these clays might be cost-effective adsorbents that could replace the costly resins which are now used for wastewater treatment. In addition examine the Ni movement with the soil columns. The solid phase of Ni by different segments of natural clays treated with sandy soil and measured by using sequential extraction as a function of soil depth.

2 Materials and Methods

2.1 Clay samples and analysis

Two natural clay deposits used were collected from different geographical locations of Saudi Arabia. The collected samples were particularly different in terms of mineral composition and CaCO₃ content. The first sample was collected from Mount Al-Mhawes, El-Kharg prefecture and the second sample from Jeddah prefecture. The collected clay samples were crushed by a ball mill to obtain grain sizes near 2 mm. Clay samples were characterized by X-ray diffraction for crystallography of the clays platelets. The chemical analysis of these clays was determined by ICP-AES spectrometry (Table 1). A sandy soil sample was collected from surface layer (0–30 cm depth) from Thumama, Riyadh Government. The soil samples were washed by hydrochloric acid to remove calcium carbonate and then washed with water to remove excess of salts and further analysis were carried out.

2.2 Adsorption experiment

Adsorption experiment was carried out by equilibrating 5.0 g soil mixed with different amount of natural clay (0, 3, 6 and 9%) with a volume of 20 mL of mixed solution contains different concentration of Ni ranging from zero to 200 mg L⁻¹ (prepared from chlorite salts). The initial pH of mixed solution was adjusted to be 6±0.1 by NaOH or HCl solution. The suspension was shaken for 24 hrs at room temperature, then centrifuged and the level of Ni and equilibrium pH in the supernatant was determined by ICP-AES. The quantity of Ni retention was calculated as the difference between initial and equilibrated Ni concentration. Langmuir and Freundlich models were used to estimate the Ni adsorption parameters.

The Langmuir equation is as.

$$X = X_m kC / (1 + kC)$$

where X = Amount of Ni adsorbed per unit mass of clay samples (mg g^{-1}), k = A constant related to binding energy (L g^{-1}), X_m = Maximum Ni adsorption (mg g^{-1}) and C = Equilibrium Ni concentration (mg L^{-1}). Nickel adsorption data was plotted according to the linear form of the Langmuir equation

$$C/X = 1/X_m k + C/X_m$$

Freundlich equation is as follows

$$X = k C^{1/n}$$

Where X is the amount of Ni adsorbed per unit mass of clay samples (mg g^{-1}), C is the equilibrium concentration of Ni in the bulk solution (mg L^{-1}), whereas k and n are empirical constants. The adsorption nickel data was plotted according to Freundlich linear form

$$\text{Log } X = \text{Log } k + 1/n \text{ Log } C.$$

Table 1 Characterization of the natural clay deposit used.

Property	Al-Mhawes	Khulais
pH (H ₂ O)	7.33	7.18
EC (dS m ⁻¹)	26.1	44.3
Cations & Anions (meq L ⁻¹)		
Ca ⁺⁺	55.5	81
Mg ⁺⁺	166	265
Na ⁺	60.5	57
K ⁺	1.89	0.96
HCO ₃ ⁻	2.50	2.50
Cl ⁻	197	408
SO ₄ ²⁻	39.5	49.7
CaCO ₃ (%)	7.0	3.0
CEC (Cmol kg ⁻¹)	36.4	71.5
SAR (%)	21.8	31.9
Texture	clay	clay
Surface area (m ² g ⁻¹)	395	691

2.3 Column experiment

This experiment was carried out to know the ability of collected clay deposit samples to remove Ni from contaminated water. The columns were constructed from polyvinyl chloride plastic columns (5.08 cm internal diameter and 30 cm length) with an end cap drilled for an outlet, which was covered with a layer of pre-washed cheesecloth to prevent the escape of soil particles. The columns were first filled up to a height of 10 cm with sandy soil, followed by 10 cm (carpet like layer) of the following treatments:

- (1). Control treatment (100% sandy soil).
- (2). Mixture of 3% Clay deposits with 97% sandy soil.
- (3). Mixture of 6% Clay deposits with 94% sandy soil.
- (4). Mixture of 9% Clay deposits with 91% sandy soil.

The final height of the soil in each column was 20 cm with an approximately bulk density of 1.65 g cm^{-3} . The treatment was arranged in completely randomized block design (CRD) with three replications. Columns

were subjected to intermittent leaching for five times (one pore volume each) using an artificially Ni contaminated water. The Ni concentration ranged from 0, 5 and 10 mg L⁻¹). At the end of the experiment, each soil column was divided into 4 segments of 0–5, 5– 10, 10–15 and 15–20 cm. The soil samples were air dried, and ground to pass through a 2 mm sieve and analyzed for total Ni by ICP-AES spectrometry.

3 Results and Discussion

3.1 Characterization of clay adsorbents

The physical and chemical properties of clay samples are presented in Table 1. The mineral composition of clay samples indicated that the natural clay deposit samples are mainly composed of percentages of the mineral present as follows: Kaluias clay with smectite 78.9%; kaolinite 6.95%; quartz 7.80% and feldspar 5.50%, while Al-Mahwes clay sample contains smectite 41.3%; kaolinite 24.4; quartz 28.1% and feldspar 5.50%. The above mentioned results indicate the dominance of smectite, kaolinite and some accessory clay minerals. Furthermore, chemical analyses show that surface area and cation exchange capacity of the natural clay samples is very high, which means that the expected adsorption process will be very fast.

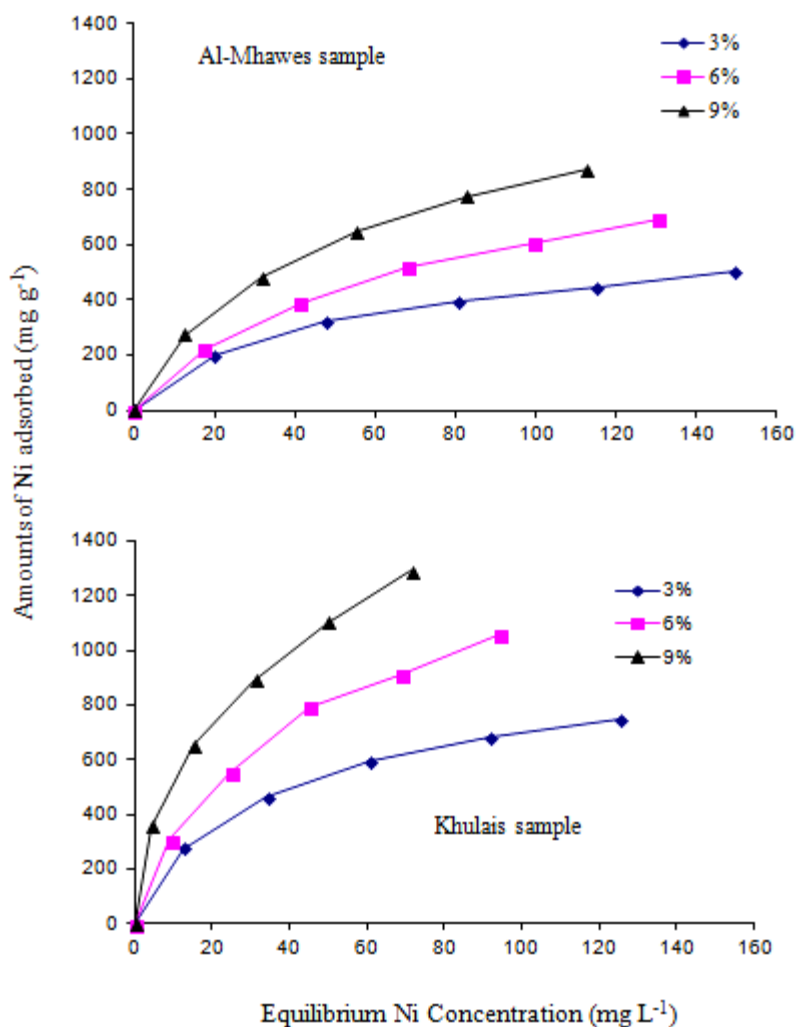
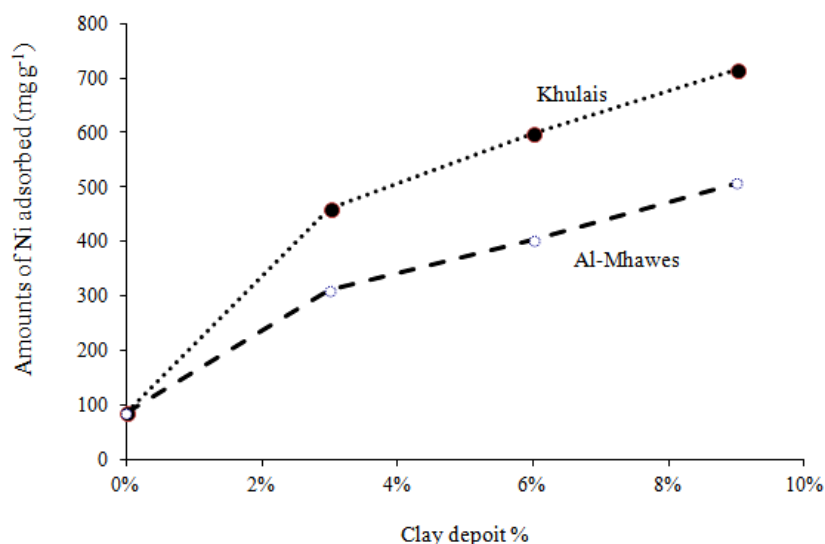


Fig. 1 Nickel adsorption isotherms on two natural clay deposit.

Table 2 Langmuir and Freundlich parameters of nickel adsorption on the two clay samples.

Deposit type	Langmuir Equation				Freundlich Equation			
	$C/X = 1/X_m k + C/X_m$				$\text{Log } X = \text{Log } K + 1/n \text{ Log } C$			
	Equation	R ²	K L gm ⁻¹	X _m mg g ⁻¹	Equation	R ²	n L gm ⁻¹	k mg g ⁻¹
Sandy Soil	$C/X = 0.0162x + 0.4431$	0.68	61.7	0.036	$\text{Log } X = 0.2737x + 1.1181$	0.30	3.65	13.1
Khulais 3%	$C/X = 0.0012x + 0.0203$	0.96	833	0.059	$\text{Log } X = 0.4358x + 1.9793$	0.98	2.29	95.3
Khulais 6%	$C/X = 0.0009x + 0.0154$	0.91	1111	0.058	$\text{Log } X = 0.5289x + 1.9916$	0.99	1.89	98.0
Khulais 9%	$C/X = 0.0007x + 0.0077$	0.94	1428	0.090	$\text{Log } X = 0.4571x + 2.267$	0.99	2.18	184
Al-Mhawes 3%	$C/X = 0.0019x + 0.0409$	0.94	526	0.046	$\text{Log } X = 0.4551x + 1.7196$	0.98	2.19	52.3
Al-Mhawes 6%	$C/X = 0.0013x + 0.0358$	0.89	769	0.036	$\text{Log } X = 0.5685x + 1.6508$	0.99	1.75	44.8
Al-Mhawes 9%	$C/X = 0.001x + 0.0219$	0.91	1000	0.045	$\text{Log } X = 0.5304x + 1.8693$	0.99	1.88	74.0

**Fig. 2** Effect of the amount of clay added on Ni adsorbed.

3.2 Adsorption isotherm

The Ni adsorption isotherms are shown in Fig. 1. These isotherms represent the Ni adsorption behavior on clays as a function of aqueous Ni concentration after 24 hours equilibrium. The isotherm indicates that the amount of Ni adsorbed by natural clay samples tends to be increases with the increase in equilibrium concentrations. At lower initial concentrations, the isotherms have a relatively high slope whereas at higher concentrations the slope was relatively low with a defined plateau for the adsorption maximum in the two clay samples. Sorption isotherms follow L-shaped type similar to that described by Sposito (1984). Such sorption behavior can be explained by the high affinity of natural clay deposits for Ni at low concentrations. With increasing amount of clays added, there is an increase in Ni adsorption. The amount of Ni adsorbed by Khulais clay sample was higher than -Mhawes, because cation exchange capacity (CEC) and surface area of Khulais clay sample is higher than the Al-Mhawes sample (Table 1). This higher CEC would, therefore lead to a higher Ni adsorption. The amount of Ni adsorbed onto clay, versus the application rate of clay added were

plotted in Fig. 2. The results showed that, Khulais clay sample exhibited the higher adsorption capacity compared to Al-Mahwes sample. This may be partly explained by differences of the chemical and mineralogical analysis between these samples. Ghoneim et al. (2002) found that the zinc and copper adsorption depends on the mineralogical composition of clay mineral, pH and species of heavy metals in the solution.

Nickel adsorption data of the two clay deposits plotted according to linear form of Langmuir and Freundlich equation (Figs. 3 and 4, respectively) and calculated constant adsorption parameters are listed in Table 2. The resulted k value tends to be increased with increasing amount of clay added to the sandy soil of both clay samples used. However, Khulais clay sample showed higher k values compared to Al-Mahwes sample. The maximum adsorption capacity varied from 0.036 to 0.090 mg g^{-1} . The n constant is related to strength of Ni adsorption, while k value is related to both strength and amount of Ni adsorbed. The data show that the n and k values increased with increasing the amount of clay added in both samples. In each case, the value n was greater than one, indicating that adsorption was favorable (Adebowale et al., 2006; Unuabonah et al., 2008). In general, the adsorption data were fitted according to Langmuir and Freundlich models with correlation coefficients ranging from 0.90 to 0.99.

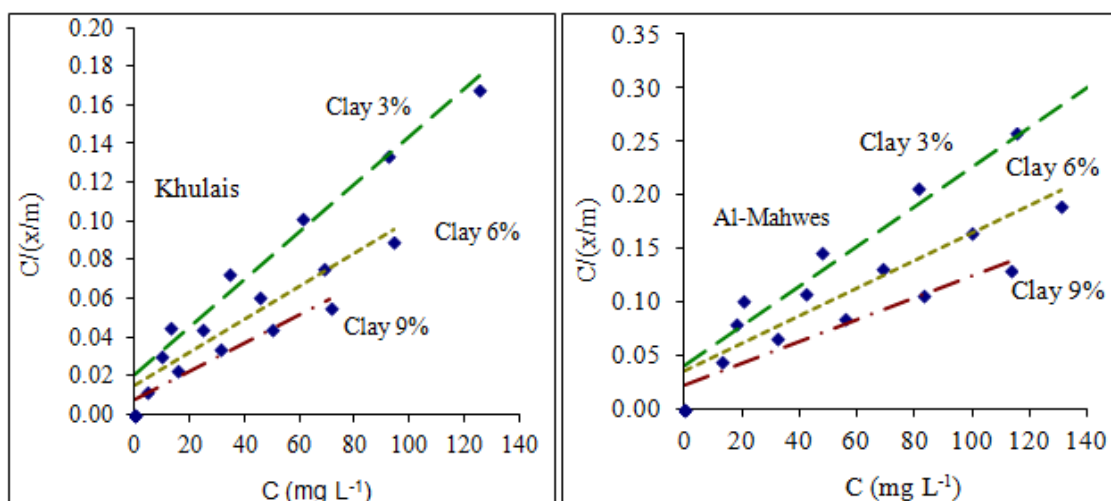


Fig. 3 Langmuir plots of Ni adsorption. C: equilibrium Ni concentration; X: amount of Ni adsorbed.

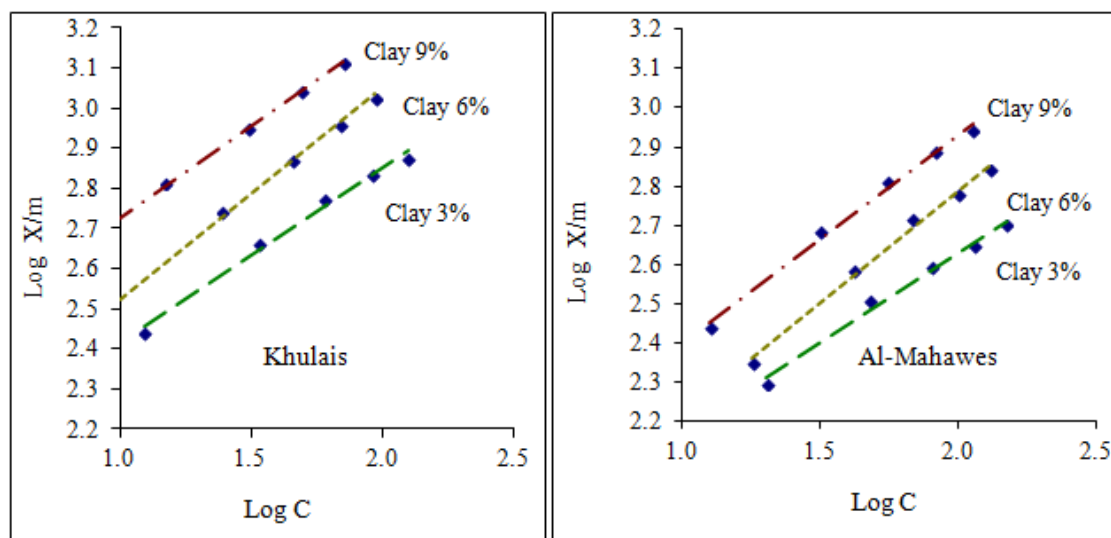


Fig. 4 Freundlich plots of Ni adsorption. C: equilibrium Ni concentration; X: amount of Ni adsorbed.

3.3 Variation in pH value

Fig. 5 shows the changes in solution pH after Ni adsorption at initial Ni concentration ranged from 0 to 200 mg L⁻¹. For each case, the pH value for the blank run (zero Ni concentration) was considered to be the initial pH value for the Ni and the two natural clay samples before adsorption. After the Ni adsorption, the equilibrium pH tended to decrease in almost all cases. By comparing the change in equilibrium pH of Khulais and Al-Mahwes sample after Ni adsorption, it can be observed that the change in pH value of Khulais is higher than that of Al-Mahwes clay sample. This fact may be related to the difference in chemical composition of the two samples and also due to that Khulais has a higher Ni adsorption capacity than Al-Mahwes. The pH effect is considered to be two factors; first, reduce in competition with protons for adsorption sites and second exposure of new adsorption sites for Ni adsorption (Ghoneim et al., 2002; Ghoneim et al., 2007 and Casagrande et al., 2008).

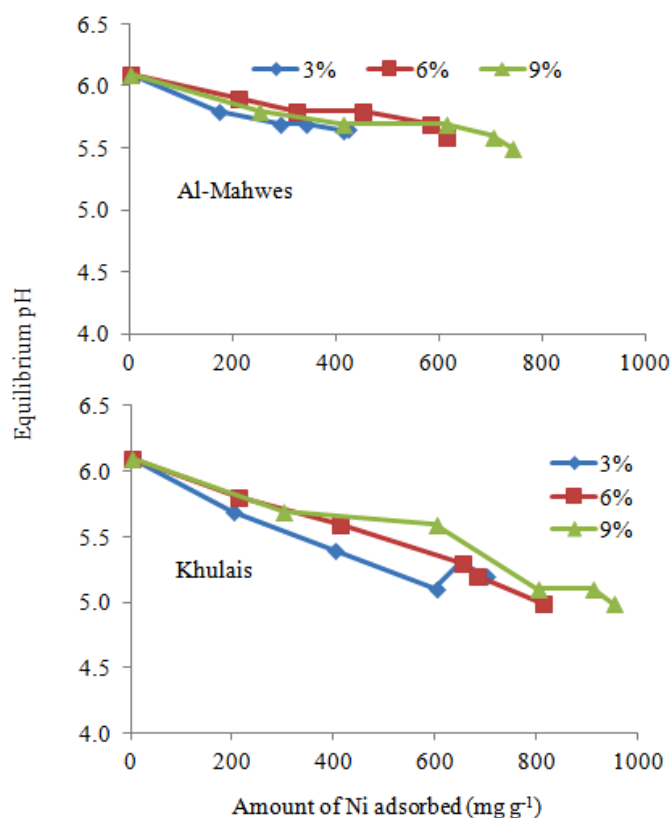


Fig. 5 Changes in equilibrium pH after Ni adsorption on two clay samples. Adjusted initial pH was 6 ± 0.1 .

3.4 Column experiment

Table 3 and 4 showed total and solid phase Ni in soil column using deposit of clay Khulais and Al-Mahwes, respectively after cuttings oil columns to four layers. The maximum exchangeable and total Ni concentration of the two clay samples were found in the surface layer (0–5 cm) and then, decreases with the increase of the soil depth. The concentration of Ni in the first soil depth was equivalent to the rate of 90–96% of the Ni added. A low mobility of Ni applied to soils was probably due to specific adsorption (Williams et al., 1985, 1987). It seems that, marked contamination of the surface soil with Ni was suggested by the higher increases in total Ni concentration found in the top soil layer compared to amounts recovered from the deeper soil depth (Table 3 and 4). The relative low Ni immobility indicates that different chemical reactions take place in the soil such as

binding with organic matter, adsorption on different iron and hydrous complexes (White and Chaney, 1980; Chubin and Street, 1981). The surface retention of Ni by the two natural clay deposits could be regulating the solubility of Ni in the soil solution and controlling its distribution between solid and solution phase. As a consequence this would help keeping Ni from being leached with drainage water.

Table 3 Distribution of different forms of Ni in sandy soil amended with Khulais clay sample.

Added clay (%)	Ni added mg L ⁻¹	Soil depth (cm)	Exchangeable Ni mg L ⁻¹	Total Ni mg L ⁻¹
3% clay	Distilled water 0	0-5	2.50	3.47
		5-10	2.43	3.50
		10-15	1.00	0.43
		15-20	0.80	0.50
	First addition 5	0-5	9.99	29.3
		5-10	0.45	5.27
		10-15	0.18	4.57
		15-20	0.17	3.93
	Second addition 10	0-5	26.7	37.3
		5-10	1.35	7.60
		10-15	0.22	4.20
		15-20	0.19	4.20
6% clay	Distilled water 0	0-5	2.90	4.40
		5-10	2.97	4.40
		10-15	0.93	1.03
		15-20	0.77	0.90
	First addition 5	0-5	19.1	27.5
		5-10	0.33	5.87
		10-15	0.15	4.33
		15-20	0.18	3.90
	Second addition 10	0-5	29.6	38.5
		5-10	1.36	9.90
		10-15	0.48	4.97
		15-20	0.27	4.43
9% clay	Distilled water 0	0-5	3.50	4.77
		5-10	3.37	4.83
		10-15	1.00	1.03
		15-20	0.83	1.03
	First addition 5	0-5	31.6	38.4
		5-10	0.31	6.80
		10-15	0.16	4.23
		15-20	0.21	4.17
	Second addition 10	0-5	50.7	56.3
		5-10	0.42	6.60
		10-15	0.15	4.37
		15-20	0.17	4.37

Table 4 Distribution of different forms of Ni in sandy soil amended with Al-Mahwes clay sample.

Added clay (%)	Ni added mg L ⁻¹	Soil depth (cm)	Exchangeable Ni mg L ⁻¹	Total Ni mg L ⁻¹
3% clay	Distilled water 0	0-5	1.30	1.80
		5-10	1.40	1.67
		10-15	0.13	0.22
		15-20	0.20	0.30
	First addition 5	0-5	10.6	16.5
		5-10	0.54	3.13
		10-15	0.08	2.70
		15-20	0.15	2.43
	Second addition 10	0-5	28.7	34.9
		5-10	3.69	6.77
		10-15	0.17	2.80
		15-20	0.22	2.17
6% clay	Distilled water 0	0-5	1.87	2.23
		5-10	1.90	2.47
		10-15	0.19	0.40
		15-20	0.21	0.73
	First addition 5	0-5	9.58	13.1
		5-10	0.26	3.0
		10-15	0.17	2.63
		15-20	0.06	2.50
	Second addition 10	0-5	38.0	48.7
		5-10	0.68	2.63
		10-15	0.15	2.47
		15-20	0.14	2.90
9% clay	Distilled water 0	0-5	2.43	3.00
		5-10	2.43	2.87
		10-15	0.30	0.50
		15-20	0.29	0.50
	First addition 5	0-5	20.7	33.3
		5-10	0.26	2.53
		10-15	0.11	2.53
		15-20	0.18	2.43
	Second addition 10	0-5	45.2	49.3
		5-10	0.60	4.80
		10-15	0.16	3.63
		15-20	0.19	4.00

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