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Chemical Behavior of some Additives used for Minimizing the Potential Hazards of Nickel in Soil

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THE PRESENT work aimed at throwing some light on chemical behavior of montmorillonite clay mineral (Mont.), calcium carbonate ($CaCO_3$) and humic acid (HA) upon equilibrating each of them with different concentrations of Ni under different pH values. Retained amounts of Ni were calculated as the difference between the applied Ni concentrations and the corresponding remained concentrations in the solution. Both Freundlich and Langmuir isotherm equations were used for describing the relationship between the adsorbed amounts of Ni per unit weight of the adsorbent and concentration of Ni in the equilibrium solution. The results revealed that the amounts of Ni adsorbed by the examined materials increased gradually with increasing concentrations of Ni in the equilibrium solution under the different studied pH values. Also, adsorbed amount of Ni per unit weight of the different studied adsorbents increased with increasing the pH values. The examined materials revealed different sorption capacities for Ni according to their nature and ambient pH value. Also, the examined materials showed different adsorption maxima as well as different affinities for Ni at the different pH values. It could be concluded from the obtained results that application of additives such like those investigated herein may be helpful in ameliorating soils contaminated with heavy metals such as Ni through changing most of its available content to retained (unavailable) content and hence limiting its transport to plant and consequently the food chain.

Keywords: Ni, Adsorption, Montmorillonite, $CaCO_3$, Humic acid.

Soil contaminated with Ni is considered a serious environmental problem. Ni toxicity appeared on plants subjected to elevated concentrations of Ni in the growth media, *e.g*., ray grass (Khalid and Tinsley, 1980), ryegrass and oats (Allinson and Dzialo, 1981), alfalfa (Taylor and Allinson, 1981), cereals (Poulik, 1997) , serpentine-endemic species and cabbage (Chaney *et al*., 2008) and plant growth in general (Seregin and Kozhevnikova, 2006 and Marques *et al*., 2009). It is worthy to mention that successive years don't affect Ni availability (Sauerbeck and Hein, 1991).

Heavy metals in general and Ni in particular can be introduced into soil and water environments from both natural and anthropogenic sources (Nicholson *et al.*, 2003, McNear *et al.*, 2005 and Egiarte *et al.*, 2008). Understanding, the associations of the different soil constituents and their affinities towards heavy metals exemplifies

the factors affecting their availability in soil (Kabata-Pendias and Pendias, 2000). Ni sorption in soil was highly affected by the clay content and the hydrous oxides of Fe and Mn (Anderson and Christensen, 1988). Also, strong fixation for Ni was also associated with goethite mineral (Gerth *et al.*, 1993). However, the sorption of Ni may be considered nonspecific on clay minerals, *i.e.,* on montmorillonite and illite clays, and specific in calcareous soil (Businelli *et al.*, 2004). Ni sorption on phyrophyllites initiated fast and decreased gradually thereafter (Scheidegger and Sparks, 1996).

pH and organic matter content are considered important factors affecting Ni adsorption in soil, with pH having the most effective factor (Scheidegger and Sparks, 1996). Also, clay minerals, *i.e.*, kaolinite and montmorillonite play important roles in Ni adsorption in soil and are strongly affected by soil pH (Gupta and Bhattacharyya, 2006, Serrano *et al*., 2009 and Regelink & Temmeinghof, 2011). This adsorption takes place mainly through surface complexation and ion exchange and is considered irreversible (Xu *et al.*, 2008 and Wang *et al*., 2012).

Clay minerals such as montmorillonite and calcium carbonate seem suitable as additives to immobilize heavy metals without affecting soil fertility negatively (Hegazi *et al.*, 2008).

Due to the abovementioned risks of heavy metals especially Ni, the current study was conducted to investigate the effect of montmorillonite clay mineral (Mont.), calcium carbonate ($CaCO_3$) and humic acid (HA) as tools for minimizing concentrations of Ni ions in soil through sorption under different pH values and different concentrations of applied Ni.

Material and Methods
Material of study
   Montmorillonite clay mineral

The clay mineral used in this study was montmorillonite. It was supplied by Sigma-Aldrich Chemical Company Inc. Its surface area is about 270 m^2g^{-1} and the cation exchange capacity is 47.53 $cmol_c$ kg^{-1}.

   Calcium carbonate

The laboratory reagent grade calcium carbonate used in this study was supplied by El-Gomhoria Company, Egypt.

   Humic acid

Humic acid was supplied by Sigma-Aldrich Chemical Company Inc.. Its total acidity is 70 c mol_c kg^{-1} and its ash content is 20%.

   Nickel stock solution

Analytical reagent grade chemical was used for preparing nickel stock solution. $NiCl_2.6H_2O$ salt was used for preparing this stock solution at a concentration of 500 mg metal L^{-1}. The pH value of the stock solution was

adjusted at either 6.0, 7.0 or 8.0 ($\pm$ 0.05) just before each adsorption experiment using 0.01 NaOH or 0.01 HCl.

The experimental work

  Montmorillonite clay mineral sorption experiment

Three suspensions of pH 6, 7 or 8 for montmorillonite were prepared by dispersing an appropriate weight of the studied material in distilled water to achieve final concentrations for the concerned montmorillonite clay mineral of 20 g L^{-1}. A set of 50 mL centrifuge reaction vessels was used, each contained 5 mL suspension, *i.e.,* 0.1 g of montmorillonite. pH values of used suspensions were adjusted previously at 6.0, 7.0 or 8.0. Appropriate amounts from the stock solutions of nickel chloride (NiCl$_2$.6H$_2$O) were added to the reaction vessels to achieve a series of final Ni concentrations of 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 µg mL^{-1} after adjusting the total volume to 25 mL per each reaction vessel by adding appropriate amount of distilled water. The reaction vessels were, tightly closed, shaken for 1hr and left for equilibrium for 24 hr then centrifuged for 30 minuets at 3000 rpm, then the supernatants were obtained.

  The calcium carbonate sorption experiment

A set of 50 mL centrifuge reaction vessels was used; each contained 0.1 g of calcium carbonate. Appropriate volumes of the Ni stock solutions of pH 6, 7 or 8 were added to the centrifuge reaction vessels and distilled water was added to adjust the volume to 25 mL to obtain a series of final Ni concentrations namely; 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 µg mL^{-1}. All vessels were shaken, equilibrated, centrifuged and the supernatants were used for measuring Ni concentrations in the equilibrium solutions as mentioned above.

  The humic acid sorption experiment

A stock suspension of humic acid was prepared as follows: An appropriate amount of humic acid was suspended in distilled water to achieve a final concentration of 5 g L^{-1}. The system was stirred continuously using a PTFE – coated magnetic stirrer. Five mL aliquots of the suspension were transferred into a set of centrifuge reaction vessels (50 mL volume each), then shaken with a series of Ni concentrations (0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 µg mL^{-1}) at pH 6, 7 and 8, equilibrated, centrifuged and the supernatants were used for determination of Ni in the equilibrium solution as mentioned above.

  Chemical analysis

Cation exchange capacity (CEC) of the used clay mineral was determined by displacing the exchangeable cations by Ba in the form of BaCl$_2$ as described by Lothenbach *et al.* (1997). Surface area of the clay mineral was determined using the procedure described by Lawrie (1961). pH values of the used Ni solutions were measured using pH meter according to Page *et al.* (1982). Nickel content in the supernatant (equilibrium solution) was determined using atomic absorption spectrophotometer (Perkin Elmer, 3300).

Data analysis

The amounts of adsorbed ion on each adsorbent, at the different used pH levels, *i.e.*, 6.0, 7.0 or 8.0, was calculated as the difference between the Ni initially added to the system and that remaining in the solution after equilibrium.

To explore the possible mechanism for Ni sorption on the studied materials, Langmuir isotherm which represents the sorption on homogenous surfaces and Freudlich isotherm which represents the sorption on heterogenous surfaces as outlined by Tan (1998) were investigated.

The general Langmuir sorption model is expressed by:

$$Qe = \frac{bK_L C_e}{1 + K_L C_e} \tag{1}$$

where Q_e is the amount of Ni sorbed by studied materials (mg g^{-1}) at the equilibrium, the parameter (b) refers to the maximum metal sorption (mg g^{-1}), C_e is the concentration of Ni in the suspension (mg mL^{-1}) at the equilibrium and K_L is the binding energy (L mg-1).

The general form of the Freundlich model is:

$$Qe = K_f C_e^{\frac{1}{n}} \tag{2}$$

where Q_e and C_e are the same as in Eq. (1), and K_f and n relate to the capacity and affinity of adsorption, respectively. The Freundlich model does not imply a saturation of the adsorptive surface.

Sorption data were modeled using the fitting curve models presented in SigmaPlot v. 10.

Results and Discussion

Sorption of Ni on the clay mineral
  Sorption of Ni as related to the initial Ni concentrations
Data illustrated in Fig. 1 revealed that Ni sorbed on the clay mineral increased as the initial applied Ni concentration increased at all the studied pH values, *i.e.*, 6, 7 and 8. On the other hand, sorbed Ni as percentage of the initial applied Ni concentration at both pH values 6 and 7 decreased whereas this percentage at pH 8 remained nearly constant at about 100% of the initial applied Ni concentrations. These results agree with those of Abollino (2008) and Bhattacharyya & Gupta (2008a) who found that montmorillonite have very high affinity for Ni and that the retention for Ni increased with increasing pH. Also, similar results were obtained by Echevrria *et al.* (2003) on illite clay mineral (another member of the smectite group) who indicated that the amounts of retained Ni increased with increasing its initial concentrations and pH. The

retention of Ni on montmorillonite could be related to the strong surface complexes of Ni on the sites of montmorillonite (Bradbury and Baeyens, 2005). Moreover, the increases in the retained Ni amounts on montmorillonite with increasing soil pH can be attributed to the corresponding increases in the pH dependent charge and consequently the CEC of the concerned clay mineral (Inoue and Satoh, 1993).
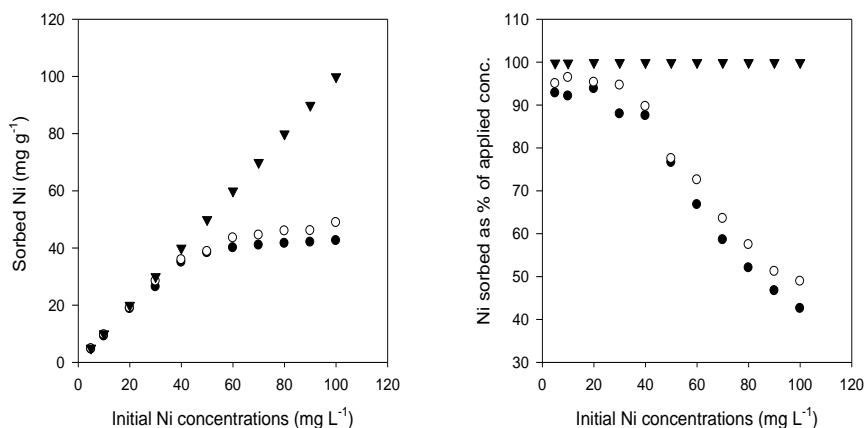
Fig. 1. Amount of sorbed Ni in relation to initial concentration of the applied Ni at pH 6●, pH 7○ and pH 8 ▼.

Sorption of Ni as related to Ni concentrations in the equilibrium solution
Values of sorbed Ni per unit weight of the adsorbent x/m corresponding to

the equilibrium Ni concentrations are illustrated graphically in Fig.2. Fitting the sorption data of Ni to Langmuir and Freudlich isotherms were also a matter of concern herein to suggest the possible mechanisms that control Ni sorption on montmorillonite clay mineral. The calculated parameters obtained from applying Langmuir and Freundlich isotherms in their linear forms are presented in Table 1. The results reveal that the values of x/m increased gradually with

increasing Ni concentration in the equilibrium concentration at all the studied pH values, *i.e.,* 6, 7 and 8. Plotting the sorption data against the corresponding equilibrium Ni concentration was found to fit both Langmuir and Freundlich adsorption isotherms at both pH 6 and 7 which confirm the responsibility of adsorption for retention of Ni at its used applied concentrations and under pH 6 and 7. However, when pH of the applied Ni was 8, the sorption data could not fit Langmuir isotherm whereas the corresponding coefficient between log C and log x/m fitted Freundlich equation. However, fitting the sorption data to the

Freundlich equation may be a false indication for the adsorption mechanisms of Ni on montmorillonite, as the equilibrium concentrations of Ni were too low to verify such a mechanism.
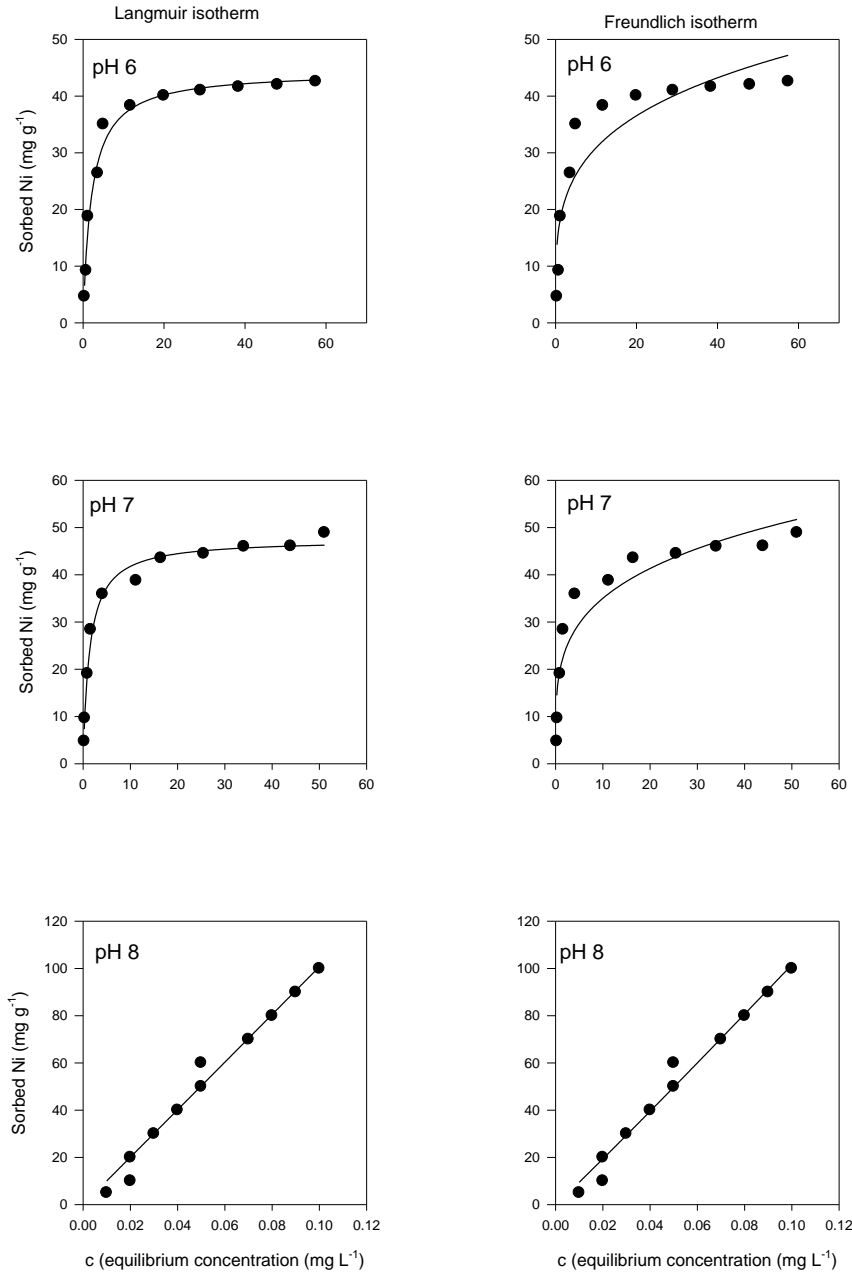
Fig. 2. Adsorption of Ni by montmorillonite according to Langmuir and Freundlich isotherm equations .

Data presented in Table 1 reveal that the Langmuir isotherm is a better model to describe Ni sorption on montmorillonite. Values of Ni maximum adsorption (b) and binding energy (k) increased with increasing pH of the applied Ni from 6 to 7. The effect of pH on increasing the affinity of Ni sorption on montmorillonite was documented by Abollino *et al.* (2003), Gupta and Bhattacharyya (2006) and Bhattacharyya & Gupta (2008b). These results agree with Gupta and Bhattacharyya (2006) who found that adsorption of Ni on montmorillonite clay mineral under different pH values fitted well Langmuir isotherm with capacity factor of 2.75 to 21.14 mg g^{-1}; while the corresponding values obtained by (Sen Gupta and Bhattacharyya, 2008) were 21.1-31.1 mg g-1. The negative value of the maximum adsorption parameter (b) calculated from the Langmuir isotherm, in addition to the high values of the capacity of adsorption (K_f) calculated from Freundlich equation 788.860 mg Ni g-1 montmorillonite which is equivalent to 0.79 g Ni adsorbed on one gram montmorillonite are not reasonable and make us reject these two isotherm models for indicating Ni sorption mechanism on montmorillonite at pH 8. Harter (1983) mentioned that hydrolyzation of the metal ion takes place under this relatively high pH. Therefore, the affinity of the adsorptive sites towards these hydrolyzed ions decreased and therefore the rate of precipitation increased in soil.

TABLE 1. Langmuir and Freundlich isotherm parameters for Ni sorption on montmorillonite clay mineral

pH	Langmuir constants			Freundlich constants		
	b	K_L	r^2	K_f	n	r^2
6	10.989	0.450	0.999	3.013	2.65	0.906
7	12.346	0.516	0.998	3.715	2.82	0.911
8	-22.106	-6.383	-0.602	788.860	0.71	0.979

Sorption of Ni on CaCO$_3$

Sorption of Ni as related to the initial Ni concentration

Figure 3 shows that increasing initial concentration of the Ni applied to the CaCO$_3$ was associated with increases in amount of sorbed Ni and at the same time, decreases in Ni sorbed as a percentage of the applied Ni concentration at both pH values of 6 and 7 whereas at pH 8 it seemed that this percentage was almost constant and did not depend on concentration of the applied Ni. Ni retention by CaCO$_3$ is mainly related to the high pH values attained due to the presence of carbonate besides the surface complexation of Ni on CaCO$_3$ (Balba, 1993 and Businelli *et al.*, 2004).
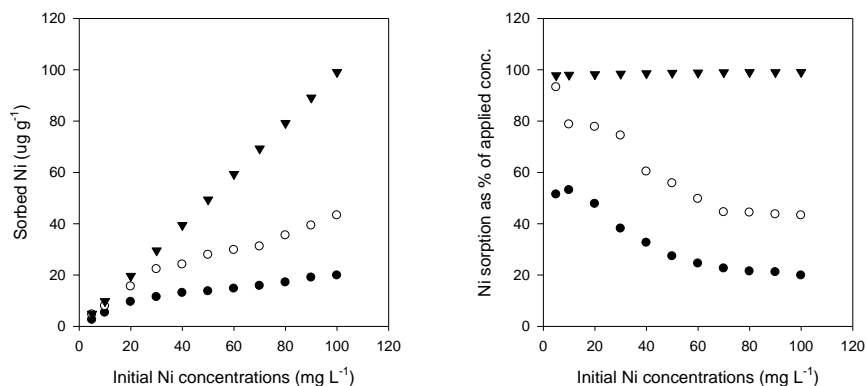
Fig. 3. Amount of sorbed Ni in relation to initial concentration of the applied Ni at pH 6●, pH 7○ and pH 8 ▼.

*Sorption of Ni as related to Ni concentrations in the equilibrium solution*
Data illustrated by Fig. 4 reveal that x/m values increased due to increasing
concentration of Ni in the equilibrium solution. Values of the sorbed Ni per unit
weight of $CaCO_3$ were progressively increased by increasing pH of the applied Ni.

Langmuir and Freundlich fitting isotherm parameters calculated at pH 6, 7
and 8 are presented in Table 2. Data show that fitting occurs at both the pH 6
and 7 for the Langmuir equation and at all the pH values of the Freundlich
equation. Based on the highest correlation coefficient values, Freundlich
isotherm seemed to be better for describing Ni sorption on $CaCO_3$. The capacity
of Ni adsorption (K_f) by $CaCO_3$ calculated at pH 7 is somewhat higher than the
corresponding one obtained at pH 6. Also, the parameter (n) exhibits higher
affinity for Ni sorption at pH 7 than at pH 6. Referring to Ni sorption data at pH
8, the capacity coefficient (K_f) recorded considerable increases for Ni sorption
compared with their values at pH 6 and 7, while the calculated affinity constant
(n) was lower at pH 8 than the calculated values at pH 6 and 7. These results
demonstrate that high sorption with low affinity takes place for Ni sorption on
calcium carbonate at pH 8. Zachara *et al.* (1991) used $Ni(OH)_2$ in determining
Ni solubility and sorption on calcite. Postulating that the following equation
controls Ni solubility under different pH values is
$Ni^{2+}(aq.) + 2H_2O(l) \Leftarrow Ni(OH)_2(s) + 2H^+(aq.)$. The increase in the pH value
neutralizes the H^+ ions resulted from this equation driving the equation forwards
towards further precipitation of $Ni(OH)_2$ and reduction in soluble Ni^{2+}
concentrations. According to Tan (1998), Gibbs free energy was calculated
from the following equation: $\Delta G_r = \Delta G^\circ_r + RT \ln K$, where ΔG_r is the free energy
change of the reaction , ΔG_r° is standard free energy change of reaction, R is the
gas constant, T is the absolute temperature and K is the activity ratio. Therefore,
the calculated Gibbs free energy of Ni precipitation as a function of pH is

$$\Delta G_r = \Delta G^{\circ}{}_r + RT \ln K = \Delta G^{\circ}{}_r + RT \ln \frac{(H^+)^2}{Ni^{2+}}$$. Ni sorption on calcite is thought to

be specific (Businelli *et al.*, 2004, Jalali and Moharrami, 2007) but the increase in soil pH (reduction in H$^+$ activity) causes a decease in the Gibbs free energy of Ni ions, and hence tends to further non specific adsorption or precipitation .
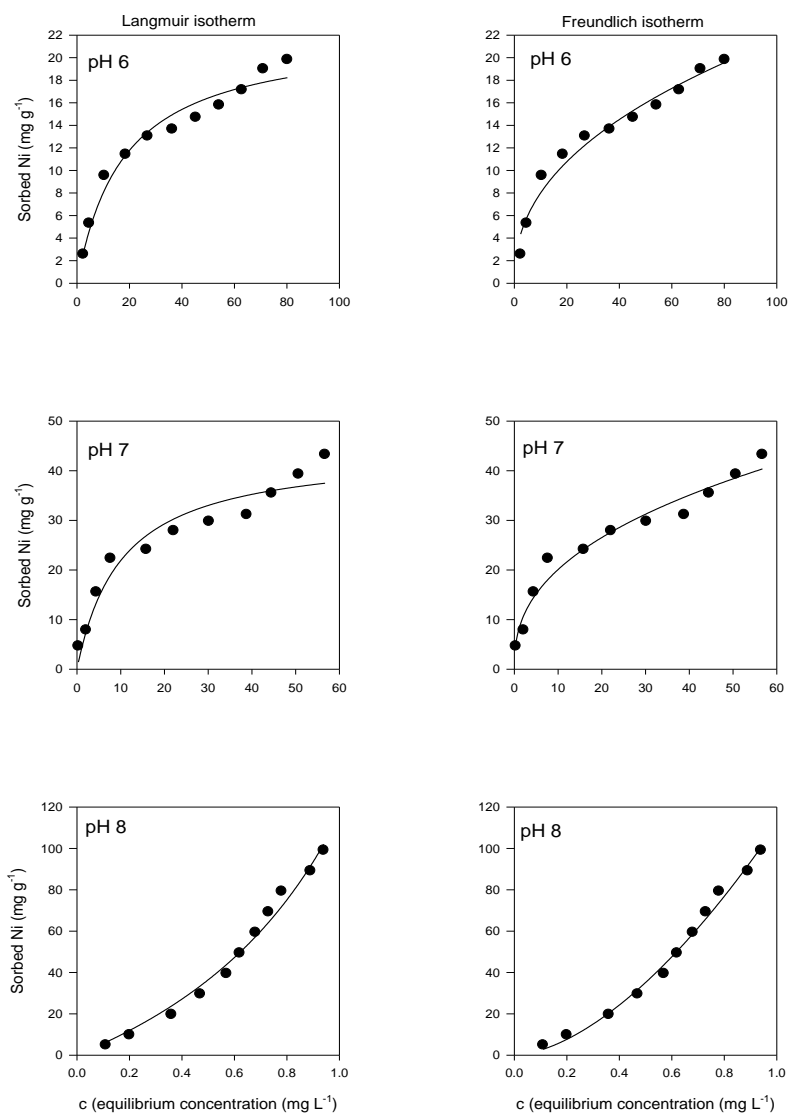
Fig. 4. Adsorption of Ni by CaCO₃ according to Langmuir and Freundlich isotherm equations .

TABLE 2. Langmuir and Freundlich isotherm parameters for Ni sorption on CaCO$_3$.

pH	Langmuir constants			Freundlich constants		
	b	K$_L$	r^2	K$_f$	n	r^2
6	5.747	0.052	0.974	0.546	1.940	0.943
7	11.111	0.104	0.948	1.822	2.330	0.968
8	-14.490	-0.713	0.978	2.5316	0.689	0.988

Sorption of Ni on humic acid

   Sorption of Ni as related to the initial Ni concentrations

   Data illustrated in Fig. 5 reveal that applied Ni at pH values of 6, 7 and 8 was associated with increases in the amounts of sorbed Ni (ug g^{-1}) and at the same time, decreases in Ni sorbed as a percentage of the initial applied Ni concentration at both pH values of 6 and 7 while at pH of 8, Ni sorbed as percentage of the applied initial Ni concentration increased with the initial Ni concentration up to 50 ug mL-1and seemed relatively constant thereafter. The highest Ni sorption rates related to the initial applied Ni were obtained at pH 8 and seemed nearly linear, followed by the sorption rate at pH 7 then pH 6.
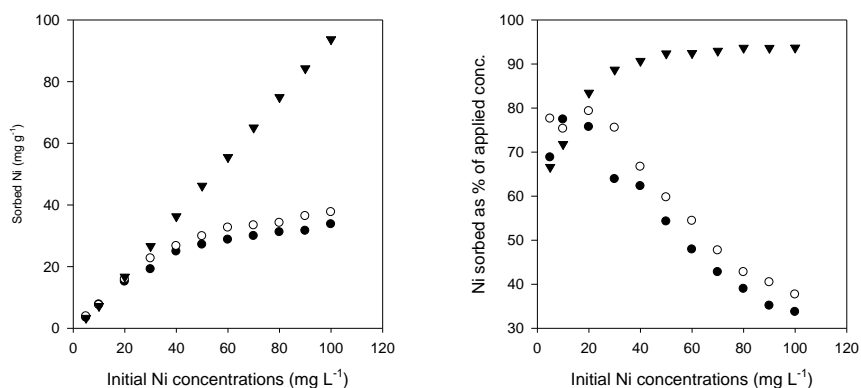

Fig 5. Amount of sorbed Ni in relation to initial concentration of the applied Ni at pH 6●, pH 7○ and pH 8 ▼.

   Sorption of Ni as related to Ni concentrations in the equilibrium solution

   Figure 6. shows that sorbed Ni per unit weight of the adsorbent x/m increased with increasing Ni concentration in equilibrium solution; also, the x/m values increased with increasing pH of the applied Ni. This means that the ability of the humic acid to sorb Ni ions in appreciable amounts on its functional groups increased with increasing the pH of the applied Ni solution which seemed to modify the ionization of carboxyl groups. These results agree with Yang *et al.*(2009) who found that the presence of humic acid increased Ni sorption. Humic acid acts as

a polyanion, the ionization of carboxyl groups is the main source of its negative charge, and the extent of its ionization is pH dependent (Stevenson, 1982), besides the formation of stable complexes were formed with Ni through coordination with hydroxyl-, phenoxyl-, and carboxyl-reactive groups for the humic acid (Pandey *et al.*, 2000) and the efficiency of metal sorption tends to increase with the increase in pH within the acidic medium (Kerndorff and Schnitzer, 1980).
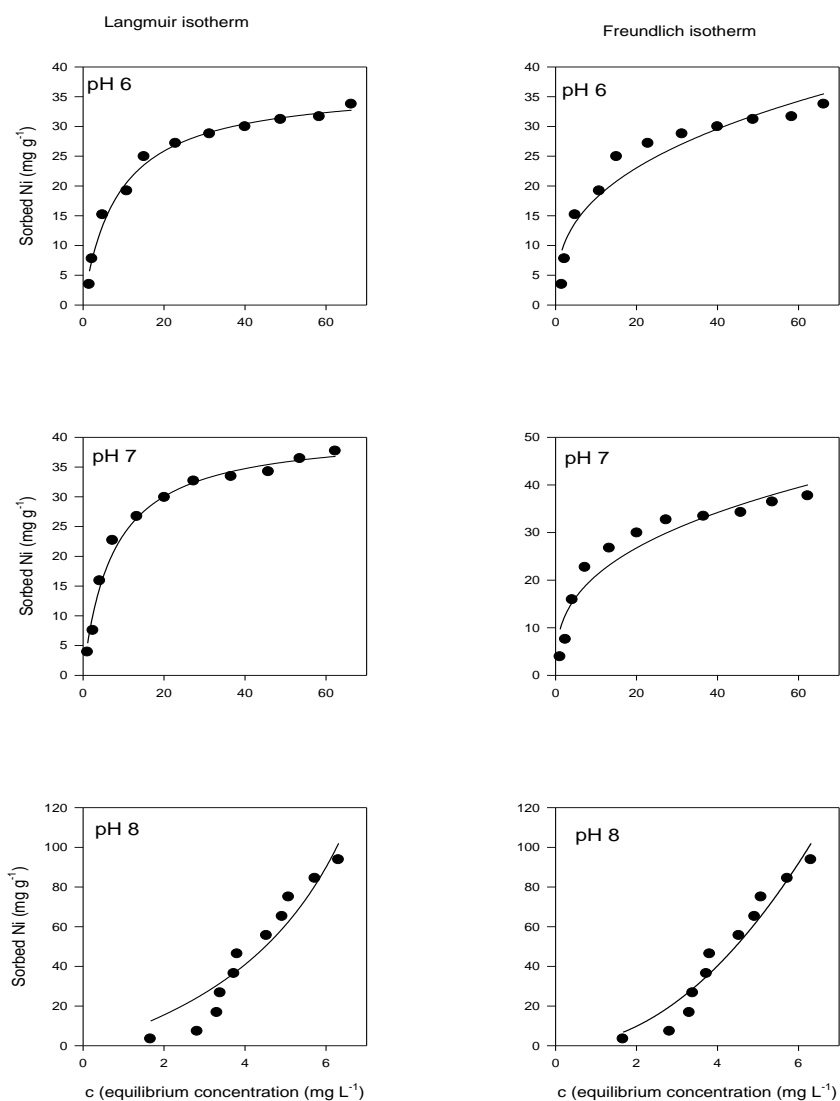
Fig. 6. Adsorption of Ni by humic acid according to Langmuir and Freundlich isotherm equations .

Data presented in Table 3 show the constants of Langmuir isotherm calculated at pH 6 and 7 and the corresponding ones calculated at all the pH values of the applied Ni solutions. Based on the highest values of the correlation coefficients, the sorption behavior of Ni ion at pH 6, 7 and 8 could be described well by Freundlich adsorption isotherms rather than Langmuir adsorption isotherm. The capacity for Ni sorption calculated by Freundlich increased with increasing pH from 6 to 7, while the affinity constant remained nearly unchangeable. On the other hand, capacity and affinity obtained at pH 8 were much lower than corresponding parameters at pH 6 and 7. These results agree partially with Yang *et al.* (2009) who found that Ni adsorption on humic acid increased with increasing pH value up to pH 8 and decreased thereafter. However, the turn point of pH value in our results was found to be 7 rather than 8 and affinity as well as capacity for Ni adsorption declined sharply thereafter.

TABLE 3. Langmuir and Freundlich isotherm parameters for Ni sorption on humic acid

pH	Langmuir constants			Freundlich constants		
	b	K_L	r^2	K_f	n	r^2
6	38.124	0.098	0.995	4.720	1.950	0.936
7	42.390	0.112	0.997	5.536	1.940	0.941
8	-11.117	0.169	0.815	0.740	0.360	0.964

The results indicate that surface affinities for Ni adsorption were as follows: montmorillonite > $CaCO_3$> humic acid and these results agree partly with Green-Pedersen *et al.* (1997) who found that the surfaces affinities for Ni adsorption for humic acid ∼montmorillonite > $CaCO_3$.

Conclusion

The studied adsorbents, *i.e.,* montmorillonite, calcium carbonate and humic acid can be used as additives to minimize concentration of Ni that might introduce the soil due to the different anthropogenic activities, however these adsorbents can deal with soils of relatively low concentration of Ni because their efficiencies in this concern are controlled by their adsorption maximum.

The maximum adsorption of Ni reveal that the tested adsorbents have ability to retain Ni and consequently reduce its concentration in soil solution dependent on pH of the media. Increasing pH of the polluted soil may be helpful in increasing efficiency of the adsorbents to reduce Ni concentration in the soil solution.

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السلوك الكيميائى لبعض المضافات المستخدمة للحد من أخطار النيكل المحتملة فى التربة

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قسم الأراضى – كلية الزراعة – جامعة بنها – بنها و*معهد بحوث الأراضى والمياه والبيئة – مركز البحوث الزراعية – الجيزة – مصر .

استهدفت هذه الدراسة إلقاء بعض الضوء على السلوك الكيميائى لمعدن طين المونتموريللونيت وكربونات الكالسيوم وحامض الهيوميك عند إضافة تركيزات مختلفة من النيكل إلى كل منهم تحت قيم مختلفة من رقم الحموضة وقد تم حساب الكمية الممسوكة من النيكل كفرق بين تركيزات النيكل المضافة والتركيزات المقابلة فى محلول الإتزان. و استخدمت معادلتى لانجمير وفروندلخ لوصف العلاقة بين كمية النيكل المدمص على وحدة الكتلة من مادة الإدمصاص (المونتموريللونيت وكربونات الكالسيوم وحامض الهيوميك) وتركيز النيكل فى محلول الإتزان. وقد أوضحت النتائج أن كمية النيكل المدمصة بواسطة المواد موضع الدراسة قد إزدادت تدريجياً بزيادة تركيز النيكل فى محلول الإتزان (تحت جميع قيم أرقام الحموضة المستخدمة) كما إزدادت أيضاً بزيادة رقم الحموضة.

تباينت مواد الدراسة فى قدرتها على إدمصاص النيكل تبعاً لطبيعتها ورقم الحموضة كما أنها أعطت قيما مختلفة لأقصى إدمصاص من هذا العنصر عند أرقام الحموضة المختلفة. ومن ثم فإنه أمكن استنتاج أن المضافات المستخدمة فى هذه الدراسة قد يكون لها دور مساعد فى علاج الأراضى الملوثة بالعناصر الثقيلة مثل النيكل وذلك من خلال تحويله من الصورة الميسرة إلى الصورة المقيدة (الغير ميسرة) ومن ثم الحد من إنتقاله إلى النبات ثم إلى السلسلة الغذائية.ً