

# Factors governing chemical behaviour of some trace elements in soil

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**SUMMARY** The present work aimed at throwing light on effect of some factors controlling chemical behaviour of both the trace elements nickel and cobalt in soil. Executing such a work required dealing with a soil as a whole beside its separated clay fraction as well as some components that are thought to be similar to the active soil constituents such as the clay minerals kaolinite and montmorillonite,  $\text{CaCO}_3$  and humic acid. These parameters together with pH value could be considered as the main indigenous factors affecting chemical behaviour of elements in soil. In addition, concentrations of the concerned elements might contribute to specify the type or types of the chemical reactions that dominate. As the trace elements are found in very minute amounts, the dominant reaction expected to dominate is adsorption, precipitation reactions may take place also. Release or desorption of the previously retained trace elements would be also a matter of concern in the current work. The experimental work, therefore, involved two main series of experiments, the first dealt with studying effect of the aforementioned factors on retention (mainly adsorption) of the considered trace elements applied at different concentrations under different pH values whereas the second dealt with release of the adsorbed elements using DTPA as a chemical extractant that has been proved by many investigators to extract what could be considered available contents of the studied trace element. In the adsorption experiments, an appropriate portion of each of kaolinite, montmorillonite surface soil sampled from Moshtohor (Qalubia), humic acid or  $\text{CaCO}_3$  was placed in a 50 mL centrifuge reaction vessel. Appropriate amounts from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  solution previously adjusted at pH 6, 7 or 8 was added to the reaction vessels to achieve a series of final Ni or Co concentrations of 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100  $\mu\text{g mL}^{-1}$ . The reaction vessels were tightly closed, shaken for one hour and left to equilibrate for 24 h. then centrifuged for 30 min. at 3000 rpm, thereafter, the supernatants were obtained. The amounts of Ni and Co sorbed by soil and the examined materials at the different pH levels were calculated as the differences between the added amounts and those found in the final equilibrium solution. In the desorption or release experiment the adsorbents remained after decantation of the supernatant solutions in the previously conducted adsorption studies were shaken for 2 h. with 20 mL of 0.005 M DTPA (pH 7.3) solution, centrifuged at 3000 rpm for 30 min., filtered and Ni or Co concentration in the filtrate was determined. The amounts of Ni or Co remained (not extractable by DTPA) on the different examined adsorbents were calculated as the differences between the sorbed amounts and the corresponding desorbed ones. The obtained results could be summarized as follows:

**A- Adsorption of Ni and Co at different pH values.**

- 1) Except for kaolinite clay mineral at pH 6, the amounts of Ni and Co adsorbed by the examined materials almost increased gradually with increasing concentration of the applied metals at the different studied pH values but did not achieve a constant value even at their highest applied concentrations.
- 2) Adsorbed amount of Ni or Co per unit weight of the different studied adsorbents ( $x/m$ ) increased with increasing pH.
- 3) Humic acid was of the highest adsorbing capacity, followed by montmorillonite clay mineral, while the tested soil was almost of the lowest adsorbing capacity among the different examined materials at the different pH values.

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4) The examined materials revealed different sorption capacities for both of the studied metals, according to their nature and the ambient pH value, i.e. humic acid sorbed more Co than Ni at pH 6 and pH 7, while at pH 8 the opposite was true. At pH 7, montmorillonite sorbed

more Co than Ni but at pH 6 and 8 it sorbed Ni more than Co. In spite of that, the examined soil tended to adsorb both the metal ions almost equally. 5) The adsorption data of both the studied metals by the examined materials at pH 6 and 7 conformed both Langmuir and Freundlich isotherms with high correlation coefficient, but at pH 8 they mostly fitted to Freundlich isotherms only. 6) The examined materials revealed different maximum adsorption values as well as different affinities for both the studied metals at the different studied pH values according to Langmuir isotherm equation, where the highest maximum adsorption values of both the studied metals were attained by humic acid whereas the lowest corresponding ones were attained by kaolinite clay mineral at pH 6 and 7, respectively. On the other hand, soil exhibited the highest affinities (binding energy,  $k$  parameter of Langmuir isotherm) for Co as compared with the examined materials at pH 6 and 7, respectively, and for Ni ion at pH 7, while montmorillonite reveal the highest affinity among the tested materials for Ni ion at pH 6. B) Desorption of Ni and Co ions at different pH levels. 1) Desorbed amount of both the studied metals (Ni and Co) increased gradually with increasing initial applied metal concentration levels but decreased gradually with increasing pH levels with all of the examined materials. On the other hand, retained amount (not desorbed) increased generally with increasing both of the initial applied metal concentrations and with increasing pH levels. 2) Desorbed amounts of Ni metal were generally lower than the corresponding ones of Co metal with most of the examined materials at different pH level, while the inverse were generally true with the corresponding retained ones. 3) Examined materials revealed different abilities to sorb, desorb and retain both of the studied metals at different pH levels according to their differences in nature, mode of actions as well as their buffering capacities to repulse change in the solid- water interface that can occur within the tested pH levels of the applied metal solution along with the applied concentration levels. The aforementioned results illustrate that both adsorption and desorption reactions of the trace metals Ni and Co are governed, to a large extent, by some indigenous soil parameters e.g. soil content of the clay fraction, type of the dominant clay minerals,  $\text{CaCO}_3$  and organic matter contents. PH value of the soil as well as concentration of the considered trace metals are also of important effects on adsorption of these metals. Increasing value of pH and / or concentration of the trace element might cause adsorption reaction to change into precipitation one. Consequently, results of the current study may be helpful in remediating soils and / or waters polluted with such trace metals. Also, the chemical behaviour of such studied trace elements can be predicted upon usage of low water quality such as sewage water in irrigation.

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