Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XIV, 2025
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

CLAY APPLICATION IN THE REMEDIATION OF NICKEL RICH SOIL

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Abstract

The objective of this study was to evaluate the ability of clay (nano- montmorillonite) to the remediation of natural (Ni) rich soils, having the nickel hyperaccumulator Odontarrhena calchidica test plant. The experiment was conducted in a greenhouse in a completely randomized design, with three replicates. The experiment was conducted in 2 kg plastic plot. We used four doses of clays: 0.0, 21.4, 44.3 and 64g kg^{-1}, corresponding to 0, 30, 60 and 90 t ha^{-1}, respectively. Throughout the experiment, the plants were regularly irrigated, and NPK fertilization was applied to ensure optimal growth conditions. After 60 days, the soil analyzed for total nickel in XRF and available nickel $_{DTPA}$ extraction in Atomic Absorption. The BFP and BFR of Odontarrhena chalcidica decreased significantly as a function of increasing doses of nano-montmorillonite, indicating an increase in the adsorption of nickel in the soil. However, the BFP and BFR values were high, indicating hyperaccumulation potential of O. chalcidica. Based on the results, the application of clay in agricultural nickel rich soils favors their improvement.

Key words: *clay, nano-montmorillonite, hyperaccumulator, Odontarrhena calchidica, XRF.*

INTRODUCTION

Nickel (Ni) is an essential micronutrient for plant growth but when present in high concentrations it can become toxic to both plants and the environment (Seregin & Kozhevnikova, 2006; Chen et al., 2009). Serpentine soils, which are naturally rich in nickel and derived from ultramafic rocks are particularly challenging for agriculture (Kazakou et al., 2008). These soils can lead to excessive nickel accumulation in food crops, raising health concerns and reducing agricultural productivity. Excess nickel slows plant growth, lowers yields and decreases the nutritional value of food (Marschner, 2012). Therefore, finding effective strategies to manage nickel-rich soils is crucial for sustainable farming.

A notable example of this challenge is the Tropoja region in northeastern Albania, where serpentine soils contain naturally high levels of nickel, posing risks to both the environment and local agriculture (Bani et al., 2015). Existing remediation methods, such as phytoremediation (using plants to absorb nickel) and chemical stabilization, have limitations.

Phytoremediation is a slow process, while chemical treatments can introduce new environmental risks (Kumpiene et al., 2008). To reduce nickel availability in soil remediation techniques such as the use of adsorbent materials, particularly clay minerals have been explored (Ghorbel-Abid et al., 2010; Uddin, 2017). These materials are readily available, environmentally friendly and effective at immobilizing heavy metals (Uddin, 2017). This occurs through processes such as adsorption and ion exchange, where nickel ions are replaced by other ions on the clay surface (Bhattacharyya & Gupta, 2008).

Nano-montmorillonite, a type of clay predominantly composed of smectite (90%), has proven effective in reducing the bioavailability of heavy metals, thereby limiting their uptake by plants (Wang et al., 2015).

Due to its high surface area and cation exchange capacity, nano-montmorillonite can be incorporated into soil as a conditioner to improve

Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

chemical and physical properties, particularly in sandy soils (Tako, 2015).

The objective of this study was to evaluate the ability of clay minerals to improve naturally nickel-rich soils, using the nickel hyperaccumulator plant *Odontarrhena chalcidica* as a test species. We use as amendment clay minerals extracted from soil of a distinct ultramafic regions of Albania, from Domosdova field, Prrenjas (Tako, 2015).

This research also aims to contribute to the development of sustainable and cost-effective methods for managing nickel-contaminated farmland while enhancing our understanding of nickel dynamics in soil-plant systems.

MATERIALS AND METHODS

Experimental Materials and Treatment

The study was conducted under greenhouse conditions at Sila Company, Fushe-Kruje, Tirane to investigate the effects of clay amendments on nickel availability and plant accumulation. Experiments were performed using the nickel hyperaccumulator plant *Odontarrhena chalcidica* native plant in serpentine soil of Albania. The soil collected from the ultramafic soil of Tropoja region in northeastern Albania (0-20 cm depth). From previous study we know that this soil was rich in nickel. Seeds of *O. chalcidica* came from native plants that grow up in ultramafic site of Tropoja. The experiments were conducted in 2 kg plastic containers. The plots were designed according to a randomized complete block design. The experiment was organized with four replicates for each treatment.

Each experimental unit received four doses of clay: 0.0, 21.4, 44.3, and 64 g kg^{-1}, corresponding to 0, 30, 60, and 90 t ha^{-1}, respectively. The clay was sourced from clayey soil from the main serpentine clay deposit in Domosdova field, southeast of Albania (Tako, 2015). The clay was thoroughly mixed with the soil to ensure uniform distribution (Uddin, 2017). The X-ray diffractogram of the clay minerals was performed in the Institute of Soil Research, University of Natural Resources and Life Sciences, Vienna, Austria and it is presented in Figure 1. The soil was conditioned in plastic containers, irrigated to field capacity, and incubated for 20 days. After incubation, *O. chalcidica* seeds were sown on March 1, 2024. Plant seeds were sown using a broadcast method and covered with a thin layer of soil on the surface. Throughout the growth period, water was periodically supplemented using the weighing method to maintain soil moisture at 60~70% of field capacity. Eight days after emergence, thinning was performed to maintain two plants per container. Fertilization was applied at rates of 3g of 20N: 20P: 20K to ensure adequate nutrient supply.

Soil and plant sample analyses

After 60 days of growth, plants were harvested, and soil and plant samples were collected. The plants aboveground parts and root systems were cleaned and weighed separately. The aerial parts and roots were separated, washed with deionized water, oven-dried at 80°C until a constant weight was achieved, and weighed to determine dry biomass of plants (Kazakou et al., 2008).

The dried soil and plant samples were finely pulverized and ground for subsequent analysis. The soil samples were air dried and passed through a 2 mm nylon sieve to determine soil physico- chemical properties; its pH, organic matter content, cation exchange capacity (CEC), available nickel was analysed in the Laboratory of the Department of Environment and Natural Resources at the Agricultural University of Tirana. Available nickel in the soil was extracted using DTPA and quantified via AAS (Lindsay & Norvell, 1978). Total heavy metals concentrations in soil and heavy metals in plant analyzed using X-ray fluorescence (XRF) in the Laboratory of the Department of Biology at the University of Florence, Italy.

The following parameters were assessed for plants: Bioaccumulation Factor in Plant (BFP) was calculated as the ratio of nickel concentration in the aerial parts to that in the soil (Bani et al., 2024). Bioaccumulation Factor in Root (BFR) was calculated as the ratio of nickel concentration in the roots to that in the soil (Kidd et al., 2018). Translocation Factor (TF) was calculated as the ratio of nickel concentration in the aerial parts to that in the roots (Bani et al., 2015).

Statistical Analysis

Data was analyzed using analysis of variance (ANOVA) with an F-test to assess treatment effects (Clay doses effects on BFP, BFR and Shoot Dry Biomass) (Kumpiene et al., 2008).

RESULTS AND DISCUSSIONS

Bulk mineralogy of the clay from source Domosdova field, south-east of Albania is dominated by the group of layer silicates.
We count to this group mica and all clay minerals. Accessory minerals are feldspars, pyroxenes, talc, serpentine minerals and traces of quartz (Figure 1). This clay could be the weathering product of ultramafic rocks. Semiquantitative results of clay mineralogy <2µm told us that this clay mineral is a nano-montmorillonite, absolutely dominated by smectite with about 90 %. All the other clay minerals are present in very small amounts. In this sample, the diffractograms from the various treatments are not definitive; some indicate the presence of smectite, while others also suggest the presence of vermiculite. The observed peaks are characteristic of smectite clays, serpentine as well as layer silicates, quartz and feldspars. This mineral will show a very high absorption capacity independently if it is smectite or vermiculite.

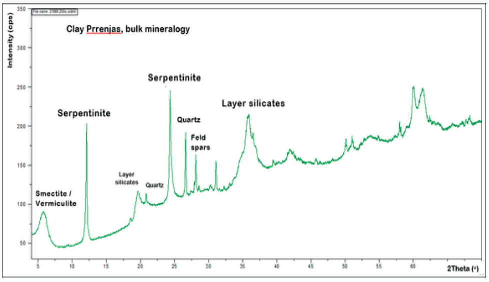


Figure 1: X-ray diffractogram of clay from Domosdova field, bulk mineral composition. The most important peaks are marked

Soil characteristics

The serpentine soil from the Tropoja region was analyzed to determine its physicochemical properties which are essential for understanding its suitability for plant growth, particularly for hyperaccumulator plants. Table 1 presents the soil properties, including pH, organic matter, texture and concentrations of essential nutrients and heavy metals.
The soil pH was neutral (7.0) that is in the adequate range for this hyperaccumulating species (Bani et al., 2014, Kukier et al., 2004). The soil of Tropoja shows a CEC of 20.6 cmol kg^{-1}, this because had a considerable clay content in the soil (27.5%).

Table 1. pH, Physicochemical properties (Mean values ± SD) of serpentine soil of Tropoja

Physicochemical properties	Mean values ± SD
pH	7
Organic matter (%)	4.5
CEC (cmol kg^{-1})	20.6
EC (µs/cm)	27.6
Sand (%)	9.95
silt (%)	62.5
Clay (%)	27.5
K (mg kg^{-1})	1442 ± 330
P (mg kg^{-1})	1859 ± 240
Ca (mg kg^{-1})	8645 ± 250
Mg (mg kg^{-1})	21867 ± 370
Cr (mg kg^{-1})	475 ± 79
Mn (mg kg^{-1})	1728 ± 13
Fe (mg kg^{-1})	96338 ± 3340
Co (mg kg^{-1})	170 ± 33
Ni (mg kg^{-1})	1739 ± 36
Cu (mg kg^{-1})	25 ± 3
Zn (mg kg^{-1})	123 ± 8
Pb (mg kg^{-1})	34 ± 4

*SD - standard deviation

Total P and K concentrations in the soil were low respectively 1442 mg kg^{-1} for P and 1859 mg kg^{-1} for K. In general, serpentine soils are deficient in K and P total contents (Bonifacio & Barberis, 1999), which is a major cause of poor agricultural yields of main crops. The use of fertilizers and organic amendments improved soil fertility.
The organic matter content was 4.5% that is satisfactory for agronomic purposes (Fenton et al., 2008). Total Ca (8645mg kg^{-1}) concentrations in the soil were lower than Mg (21867 mg kg^{-1}), and soil has elevated levels of total metals like Ni, Co, Cr, Mn and Fe that are typical of ultramafic soils. Total Ni concentration is high 1739 mg kg^{-1}, higher than those considered toxic to normal plants by Allen et al. (1974), Kabata-Pendias (1984), and Brooks (1987).

Nickel availability in soil

The application of nano- montmorillonites clay significantly reduced the bioavailability of nickel in the serpentine soil of Tropoja. As shown in Table 2, the available nickel concentration decreased with increasing clay doses.

Table 2. The available nickel in serpentine soil of Tropoja for the different clay treatments

Treatment (Clay Dose) (g/kg)	Nickel available in soil (mg/kg)
0	88.7
30	69.9
60	33.6
90	27.9

Thus, the available nickel content in the Tropoja soil, where clay from the Domosdova field was applied and nickel hyperaccumulator plants were cultivated, decreased by 68.5%, from 88.7 mg/kg to 27.9 mg/kg.
This reduction is attributed to the adsorption and ion exchange properties of nano-montmorillonites which immobilize nickel ions due to its high surface area and cation exchange capacity (CEC).

Nickel Concentrations in Plants and Roots

The dry biomass of the aerial part (shoot) of the *O. calchidica* was adjusted to a linear model as a function of increasing doses of clay mineral (Figure 2) ranged from 3.1 g (0 t ha^{-1} clay mineral) to 5.4 g (90 t ha^{-1} clay mineral), corresponding to an increase of 1.74 times higher in the highest dose compared to control.

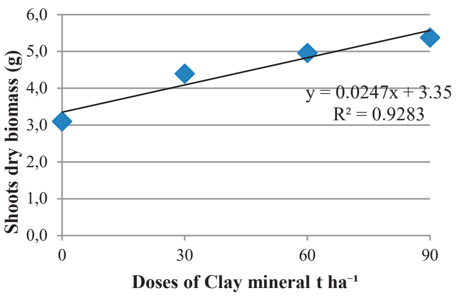
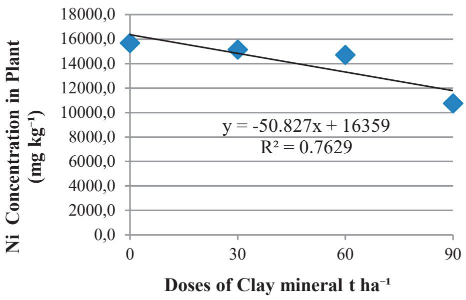
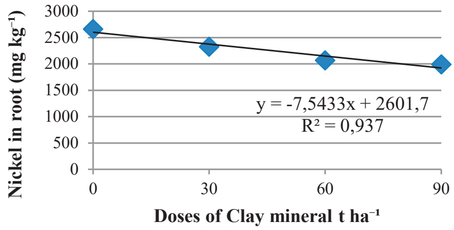


Figure 2. Dry biomass of the shoots for *O. calchidica* cultivated in serpentine soil of Tropoja for the different nano-montmorillonite clay treatments

The positive effect of nano-montmorillonite clay addition on plant growth may be due to its positive effect on the water retention capacity (Wang et al., 2015) and the growth of surface area, increasing the metal cation adsorption capacity present in the soil (Tako, 2015) and consequently decreasing the concentration in the plant parts.
The nickel concentration in the shoot and in the roots of radish was significantly influenced by applying nano-montmorillonite clay (Figure 3). The linear behavior of the nickel concentration in shoots and roots of plants, shows the decrease of Ni concentration with increasing doses of nano- montmorillonite clay ranging from 16545 to 9078 mg kg^{-1} in the shoot (Figure 3A) and ranging to 1993 to 2660 mg kg^{-1} in the roots (Figure 3B) occurring a decrease of 31.47% and 25%, respectively, the control regarding the higher dose.



A)



B)

Figure 3. Nickel concentration in the shoots (A) and roots (B) of *O. calchidica* cultivated in serpentine soil of Tropoja for the different nano-montmorillonite clay treatments

The reduction of Ni concentration in this hyperaccumulator plant is explained by the reduction of the availability of the nickel in the soil with the increase of clay doses from 0 to 90 t ha^{-1}. This decrease is likely attributable to the adsorption of nickel by nano-montmorillonite. The ability of a plant to accumulate metals from soil can be estimated using the bioaccumulation potential in plant (BFP) and/or in root (BFR). These factors can be used to estimate a potential

plant for phytoremediation purposes. The BFP and BFR of *O. calchidica* decreased significantly by increasing doses of nano-montmorillonite soil (Tables 1, 3) indicating an increase in the adsorption of nickel in the soil, decreasing the concentration in the plant parts.
This behavior is beneficial since clay minerals such as nano- montmorillonite have a great potential to adsorb pollutants due to their large specific surface area, the layered structure, and high cation exchange capacity (Bhattacharyya & Gupta, 2008).
According to Figure 4, the BFP and BFR ranged from 9 to 6.17 and from 1.52 to 1.14 showing a reduction of 31% and 25%, respectively. The BFP and BFR values were high, indicating high hyperaccumulation potential of *O. calchidica*, for Ni. Application of nano- montmorillonite reduced BFP and BFR values indicating reduced nickel uptake. These results suggest that nano-montmorillonite is an effective amendment for reducing nickel bioavailability in nickel-rich soils.

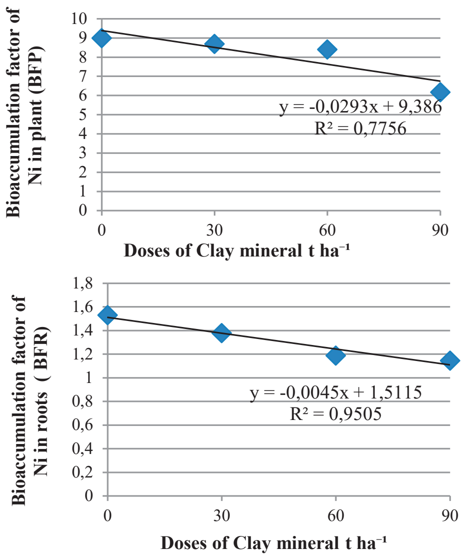


Figure 4. Bioaccumulation factor of nickel in plant (BFP) and in root (BFR) of O. calchidica for the different nano-montmorillonite clay treatments

The translocation factor (TF) gives the shoot/root nickel concentration and showed the ability of our plant for nickel translocation from roots to shoots at our experiment with different doses of clay minerals.

Table 3. Clay doses effects on BFP, BFR and Shoot Dry Biomass tested one-way ANOVA

Variable	F-value	P-value	F crit
BFP	25.61	0.000187	4.066
BFR	118.01	5.82E-07	4.066
Shoot Dry Biomass	46.9	2.02E-05	4.066

The TF varied from 7.1 to 5.89 showing a reduction of 17% depending on Clay doses. However, TF values were high, indicating high nickel translocation potential of *O. calchidica* plant.

CONCLUSIONS

Nano-montmorillonite in nickel-rich soil significantly enhanced the shoot development of *Odontarrhena calchidica* and promoted nickel retention in the soil, as evidenced by reduced nickel concentrations in the plant's shoots and roots. It also contributed to the reduction of bioaccumulation factors of nickel.
This study highlights the vital role of nano-montmorillonite clay in making nickel-rich soils safer and more productive. By applying this clay, the bioavailability of nickel is significantly reduced, protecting crops and the food chain from harmful accumulation.
The notably high nickel concentrations in the aerial parts of *O. calchidica* further confirm its strong hyperaccumulation ability, making it highly suitable for phytoremediation.
These findings are not only scientifically significant but also offer practical solutions for farmers and communities dealing with nickel-rich soils.
By improving soil health and reducing nickel toxicity, this approach supports healthier crops, sustainable agriculture, and public health. Future research should examine the long-term effects of clays and the use of *Odontarrhena calchidica* to enhance remediation efforts.

ACKNOWLEDGEMENTS

Special thanks to the technical staff of the three laboratories that assisted us with all analyses presented in this paper: the Laboratory of the Department of Environment and Natural Resources at the Agricultural University of Tirana, the Laboratory of the Institute of

Applied Geology, Department of Civil Engineering and Natural Hazards in Austria, and the Laboratory of the Department of Biology at the University of Florence, Italy.

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