# Soil Remediation by Removal of Cu and Ni with an Unconventional Organic Solution

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### Abstract

The contamination of soils with toxic metals is a major ecological concern, especially in close vicinity of automobile workshops. This study focuses on the extraction of copper (Cu) and nickel (Ni), using 2, 4-pentanedione (Hacac) dissolved in a non-polar organic solvent (methylated spirit). The objective of the investigation was to investigate the target metals' mobilization and its secondary Fe mineral dissolution induced by the soil washing treatment. Operating conditions such as soil/solution ratio (1:10), acidity (pH 4.7) and extraction time (150min) were monitored during the process.

Results showed that the optimum extraction efficiency (>50%) for Cu and Ni occurred at low pH. However, the extraction process revealed a simultaneous high Fe dissolution (up to about the 35% of the total Fe content in the soil) in the form of ferric triacetylacetonate (Fe (Hacac)3) complex, suggesting that the predominant fraction of the targeted metals extracted were occluded in the Fe-Mn oxides fraction. The desorption process of the metals extracted included fast and slow phases. The kinetics of the extraction process can be described by an Elovich function (R2 values ≥ 0.93), which is typically associated with a heterogeneous diffusion process. Overall, the test result affirms the effective removal of Cu and Ni with Hacac. The high degree of iron dissolution which occurs simultaneously suggests that a bulk micronutrient chemical evaluation is essential within the soil when an extractive decontamination activity is proposed for site remediation.

**Keywords:** Heavy metals; Extraction; Leaching; Efficiency

## Introduction

Soil contaminated with heavy metals constitutes a serious environmental problem throughout the world [1]. This is most worrisome in developing countries, where intervention values are much higher than in the developed world. Various anthropogenic activities, especially automobile repairs, generate and accumulate substantial metal-bearing wastes around the vicinities where they operate [2] and this creates environmental contamination at unacceptable levels. The impact of these wastes (metals) could be potentially deleterious and could have far reaching consequences due to its mobility, toxicity and persistence in the environment and living organisms exposed to them [3,4]. Although many of these metals occur naturally in the soil, and are intrinsic elements of the earth's crust, inordinate amounts introduced into the soil can present a potential environmental and health risk, depending on the chemical forms of the metals. The latter aspect controls both its mobility and reactivity in the environment [5].

The forms and pathways presented by some of these metals have greatly increased their chances of human exposure via a source-pathway-receptor mechanism. These contaminants can persist and accumulate in plants and animals after their release into the ecological system due to their stability, biological and non-degradability potentials thereby endangering human and animal health. This phenomenon can be attributed to some of the respiratory-related diseases common in our contemporary world which invariably is implicated to the high burden of heavy metals via the food chain [6]. This exposure could result to acute or chronic diseases with concomitant effects. For instance, Ni exposure during work activity can cause bronchial asthma or other associated occupational lung diseases [7]. Animal studies in the past confirms [8] that nickels are primarily deposited in the lungs particularly when associated with insoluble NiO, followed by moderately soluble $Ni_3S_2$ and insoluble $NiSO_4$. Thus, their (Ni, Cu) removal from contaminated soils becomes critically important in the close vicinities of automobile repair shops.

Technologies used for soil remediation include, but not limited to, solidification/stabilization, thermal treatment, physical separation and froth flotation [9]. These processing techniques are associated with high costs, high energy consumptions and

high greenhouse gas emissions. However, soil washing has been developed as one of the *ex situ* conventional remediation methods for remediation of heavy metal polluted soils. It works by dissolving or suspending the undesirable soil contaminants in a washing solution, which is typically an aqueous solution of a chelating agent which allows heavy metal desorption from soil solid phase by forming strong and water-soluble metal ligand complexes. This approach does not cause deterioration of soil physico-chemical properties and it is economically efficient [10]. The most commonly used chelating agents are typically weak organic acids and the aminopolycarboxylic acids, e.g., ethylene diamine tetraacetic acid [EDTA], because of their high chelating ability and capacity to enhance the metal extraction from the soil solid phase [11,12]. However, EDTA is less efficient in extracting metals bound to the reducible/Fe-Mn oxide fraction in soils [13,14] and is practically inefficient and unavailable for metals occluded in the residual fraction of the soil [15]. This observation was corroborated by the sequential chemical extraction conducted by Lee & Kao [16]. These authors observed a higher removal efficiency of heavy metals associated with exchangeable fractions, than those strongly adsorbed onto the Fe-Mn oxides fraction. Hence, there is still a need for sustainable and effective chelating agent that has the extractive capacity to enhance metal solubility from these recalcitrant soil solid phases. Previous studies have demonstrated the enormous potential of Hacac for iron extraction from iron ore fines (11). However, the specific combined extraction of metals (Cu and Ni) from contaminated soils has not been previously reported prior to our study making our work eminently novel.

Acetylacetone ($C_5H_8O_2$), also referred to as 2,4-Pentanedione (Hacac), is a chelating agent of ß-diketones. It is a volatile ligand at room temperature with a density of 0.975g/ml, and it boils at 140℃ under atmospheric pressure. Hacac has a bidentate structure because it can bond to the central iron via both oxygen atoms.

Currently, a significant increase in environmental pollutants have occurred around soils surrounding automobile services and repair activities, as observed and reported by Nwachukwu et al. [17]. Some of the wastes occluded in the soil include wastes from solvents used for cleaning metallic parts, asbestos from brake pads, and corrosion of scrap auto panes discarded indiscriminately within the working environs. The chemical components of these wastes can be tremendously toxic when absorbed by the skin, inhale to the lungs or adsorbed in soils in the vicinity of automobile workshops. While the automobile activity is of great economic value, the ecological impact thereof has become a serious problem affecting land-use, water and public health management.

Several studies [17,18] to assess the heavy metal concentrations and the ecological and health risk associated with automobile waste in the Owerri metropolis Nigeria have been conducted in the past with no sufficient and sustainable data to date has been presented to potentially remediate or reduce the concentrations of these heavy metals in the soil to a safe threshold level. Therefore, the aim of this present work was to evaluate the soil contamination of Nekede mechanic/automotive workshop for remediation purposes by leaching of targeted metals (Cu and Ni) with an unconventional soil washing agent that are more commonly applied in mineral processing, i.e., Hacac dissolved in non-polar solvent (methylated spirits). For this purpose, a-column based configuration was adopted. The efficiency of the washing treatment, and its secondary effect on Fe dissolution in the soil, was assessed.

## Materials and Methods

### Study area

The study area, indicated in Fig.1a, is located in Nekede mechanic village, which is considered to be the largest functional mechanic village in South-Eastern Nigeria. Nekede is a town within the Otamiri watershed and ranges longitudinally between 7°03' and 7°05' and 5°26' and 5°26' in latitude. The climatic conditions of the area have the following characteristics: temperature range of 21℃ to 27℃, relative humidity ranges between 60-80%. The area lies within the sub-equatorial, sub-humid region with March to October experiencing a rainy season and November through to February experiencing a dry season. Annual average rainfall is approximately 1500mm with a monthly average rainfall of 30mm. The communities are mainly agrarians and farm within the vicinity of the mechanic village. This creates the possibility for increased levels of heavy metals across the food chain and results in bioaccumulation of the metals by living organisms.

The soil used in the study was collected from a polluted automobile site in Owerri, Imo state, Nigeria. Soil samples were randomly collected at drainage points along the natural flow direction from the site, within the auto-mechanic surrounding at each location, as shown in Figure 1b. The sample collection was done in the order of different depths, i.e. (0-15)cm, (15-30)cm, and (30-45)cm, within a 10m radius of each other, using a soil auger. The collected samples were later homogenized to make a composite sample for the area under investigation. The homogenized sampled soil was dried at 40℃ and sieved through a 2mm mesh sieve. Soil properties are shown in Table 1.

2,4-Pentanedione (Acetylacetone-Hacac) and industrial methylated spirit (IMS) used for this study were purchased from Alfa Aeser. Throughout the investigation, high purity deionized water (18.2mΩcm) was used. All glassware and Polytetrafluorethylene (PTFE) containers used were previously soaked in 10% (v/v) nitric acid for 12h and then rinsed with high purity deionized water prior to use.

Standard techniques and approaches were employed to determine the physical and chemical properties of the soil samples. Total organic content was estimated by Loss on Ignition [19]. The

pH was measured at solid: liquid ratio 1: 10 after mechanical agitation at 120 revolution min^{-1} using a reciprocating shaker for a minimum of 60min (Mettler Toledo, [20]. Specific surface area (SSA) and Cation Exchange Capacity (CEC) were measured using standard methods by Cokca & Birand [21] and Santamarina et al. [22], respectively. The particle size analysis was done with a Malvern mastersizer 2000, and the acid soluble metal content of the soil was determined after dissolution in aqua regia. The dissolved Cu, Ni, and Fe concentrations were measured with ICP-OES and sample concentrations were corrected for matrix effects by procedural blanks, normalized to sample mass and reported as mgkg[-1] dry weight.
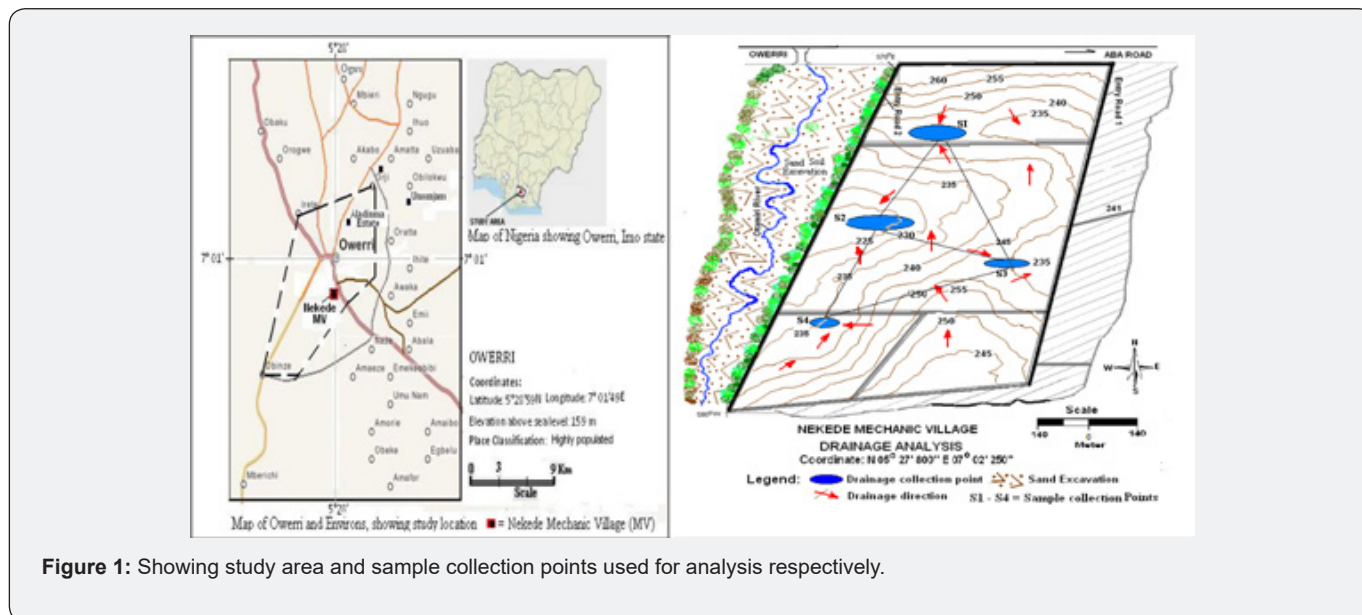


**Figure 1:** Showing study area and sample collection points used for analysis respectively.

**Table 1:** Physicochemical properties and elemental concentrations of contaminated soil with reference to regulatory limits of various heavy metals investigated as per EU and Nigerian DPR values.

| Mineral Type | Characterization | | | | Particle Size (%) | | | Elemental Concentration (mgkg[-1]) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Texture | pH | CEC | SOM | Sand | Silt | Clay | Cu | Ni | Fe |
| Kaolinite, Anatase, Quartz | Sandy loam | 4.2 | 13.67 | 2.72 | 82.54 | 7.49 | 12.55 | 155 | 75 | 19500 |
| European Union Standard (MEF, 2007) | | | | | | | | 100 | 50 | Nil |
| Nigerian Intervention value (DPR, 2002) | | | | | | | | 190 | 210 | Nil |

The column experiment was performed using an experimental setup (in triplicate) that consisted of a separating funnel as a reservoir, a glass chromatographic column (internal diameter 0.2cm and 30cm in height) equipped with a sintered disc frit to regulate flow rate. The leaching solution (80% Hacac in 20% IMS) was introduced into the column using via the reservoir and a constant head of 10cm[3] was used to deliver influent solution at a flow rate of 0.8cm[3]. min^{-1}. The soil sample was uniformly packed (8cm) using a slurry technique and sandwiched between two thin layers of sand (0.5cm) each. The leachate was collected at selected time intervals over a total leaching time of 150min. Flow and pH (4.2± 0.2) were measured immediately after sample collection. The metal concentrations (Cu, Ni, and Fe) were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) at the Manchester Metropolitan University. The concentration of Hacac ensured an excess of extractant for each of the target metals concerned. The percentage metal leached from the soil was calculated using equation [1] as follows;

$$\%metal\ leached = \frac{mass\ of\ metal\ in\ supernatant}{mass\ of\ metal\ originally\ present\ in\ soil} \times 100 \qquad Eq(1)$$

## Results and Discussion

### Soil characterisation

The soil parameters were characterized based on colour (Munsell), CEC, mineral profile, and pH as summarized in Table 1.

The soil exhibited a reddish brown colour (Munsell 5YR.5/1), which indicates the presence of red earths, characterized as ferric oxide. The CEC gave a low value (13.7), suggesting a low metal exchange capacity. This could likely influence the leaching dynamics of the soil. X-ray diffraction reveals quartz, kaolinite, and anatase as major minerals in the soil. Due to the presence of

these highly weathered clay minerals, the ability for the soil to retain cations maybe solely influenced by surface area. The pH (4.2) is acidic, which can assists metals in the two leach readily. The soil bulk geochemistry suggests that the metals of interest are present at levels higher than the EU regulatory standards, but lower than that set for DPR (Department of Petroleum Resources) values in Nigeria.

## Column extraction

*In situ* column leaching experiments with a solid: liquid ratio of 1: 10 were used to investigate the extraction behaviour of Cu, Ni, and Fe bound in and to the soil components. The leaching concentrations of metals (mgkg$^{-1}$) extracted from the contaminated soil after 30, 60, 90, 120 and 150 minutes contact time with Hacac are summarised in Table 2.

**Table 2:** Extraction and percentage efficiencies of metals leached over various times (in min).

| Time (min) | Cu (155) | | Ni (75) | | Fe (19500) | |
|---|---|---|---|---|---|---|
| | Extraction (mgkg$^{-1}$) | % Efficiency | Extraction (mgkg$^{-1}$) | % Efficiency | Extraction (mgkg$^{-1}$) | % Efficiency |
| 30 | 29.08 | | 12.68 | | 930.29 | |
| 60 | 18.74 | | 9.78 | | 1769.78 | |
| 90 | 18.62 | 56.39 | 8.49 | 53.13 | 2040.56 | 34.5 |
| 120 | 12.21 | | 5.39 | | 1060.6 | |
| 150 | 8.75 | | 3.51 | | 924.98 | |

The extraction performance of Hacac at chelant-to-metal molar ratios of 2:1 under acidic conditions is illustrated in Figures 2 (a, b, c, and d). It is clear that there are considerable differences in the metals leached (mgkg$^{-1}$) and cumulative extraction efficiencies (%) that were observed for the three metals (Cu, Ni, and Fe). Figure 2 (b, c, and d) are graphical representations of the percentage leaching efficiency for the Cu, Ni and Fe over time. For Cu, the amount of leaching indicates a downward trend, with the highest extraction occurring within 30min before eventually flattening off (Figure 2b). The total cumulative leaching is 56.4%. The leaching of Ni was observed to maintain a fairly uniform downward trend with highest extraction occurring at 30min after the start time and then it gradually flattens off (Figure 2c). The total cumulative leaching efficiency was 53.1%. However, Fe leaching exhibited a leaching trend that progressively attained a maximum peak at 90min before displaying a steep drop. The total cumulative extraction was 34.5%, which is quite a bit lower than in the cases of Cu and Ni (Figure 2d). Sequential extraction work reported by Tessier et al. [23], indicates that the extraction behaviour and amounts of each metal leached can be explained by the dominating phases commonly present in the soil, e.g., Fe-Mn oxide, exchangeable and carbonate phases. The effectiveness of Hacac to mobilize Cu and Ni within the short times observed may be attributed to its reaction kinetics, active chemical affinity and specificity of the metal-ligand interaction in the reactions [24]. The simultaneous extraction of Fe is due to the significant affinity between Hacac and Fe (Log $K_{fe-hacac}$ = 9.30). This is higher than the stability constants for Cu (Log $K_{Cu-hacac}$ = 8.24) and Ni (Log $K_{Ni-hacac}$ = 4.96) with acac [25], respectively.

**Table 3:** Parameters of the kinetic models calculated for the extraction of metals of interest from a contaminated soil using 3.00 M of Hacacat a pH = 4.7.

| Metals | Elovich | | | Power Function | | | First Order | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_t = \alpha + 1/ß \ln t$ | | | $\ln q_t = \ln a + b \ln t$ | | | $\ln (q_e - q_t) = a - k_1 t$ | | |
| | $\alpha$ | $\beta^{-1}$ | $r^2$ | a | b | $r^2$ | a | $k_1$ | $r^2$ |
| Cu | 1.64 | 6.38 | 0.93 | 2.399 | 1.09 | 0.843 | 3.07 | 0.0005 | 0.911 |
| Ni | 2.74 | 1.59 | 0.981 | 2.331 | 1.09 | 0.881 | 2.38 | 0.0001 | 0.908 |
| Fe | 1.94 | 3.96 | 0.969 | 2.311 | 1.04 | 0.89 | 2.6 | 0.005 | 0.904 |

N/B: α and ß are Elovich constants, $r^2$ is coefficient of constant determination, a and b are constants (rate coefficient value).
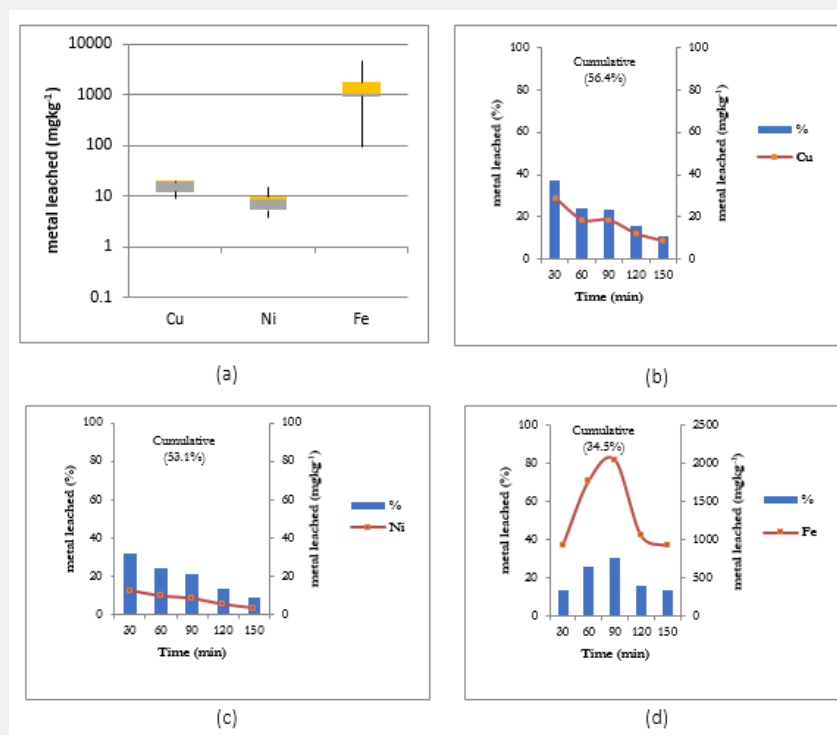
**Figure 2:**

(a) Box plot showing variation in metals leached using Hacac. The lines inside the plot represent the median values; the lower & upper boundaries indicates 25th and 75th percentiles of sample size (3).

(b) Percentage efficiency and leaching trend of Cu over time intervals.

(c) Percentage efficiency and leaching trend of Ni over time intervals.

(d) Percentage efficiency and leaching trend of Fe over time intervals.

## Kinetic studies

From the results presented in Table 2, one can deduce the kinetics of the Cu, Ni, and Fe extraction processes from the contaminated soil. Three models (Elovich, power function and $1^{st}$ order function) were fitted to the data to describe the extraction dynamics. These models are commonly used in literature [26,27]. The parameters of the three types of models are presented in Table 3. Based on the values of the regression coefficients ($R^2$) it can be concluded that the Elovich model best describes the extraction kinetic behaviour when compared to the other two models [28]. The values of α and $β^{-1}$ variables (Table 3) were typical of fast and slow desorption processes, an indication that diffused extraction may have occurred. This phenomenon often occurs during coordination interactions in the extraction process [29].

## Conclusion

The use of Hacac dissolved in methylated spirits as an unconventional soil remediation solution to extract Cu-Ni from soil at a contaminated site demonstrated an efficient process with average efficiency of >50% Cu and Ni leached. The kinetic extraction was found to involve the initial metal dissolution via pH-dependent, followed by the development of exchange reactions between the metal-Hacac complexes. The kinetics of the extraction process for the heavy metals Cu and Ni obey the Elovich equation. The kinetic model derived in this study could be utilized in the design of a reactor which can be employed for a batch remediation process. While metal recovery has not specifically been addressed in this investigation, metal recovery from the extracted M (acac)$_x$ complexes are theoretically possible via one of two routes, which will both simultaneously regenerate the Hacac extractant as part of the process. In the one instance hydrogen gas can be used as metal reactant, which would yield nano-metal particles. In the second case one can use hydrogen sulphide to first precipitate the metals as metal sulphides, and then roast the metal sulphides in a reducing hydrogen atmosphere. This will simultaneously reduce the metal and regenerate hydrogen sulphide for reuse in the precipitation step. A useful follow up of this investigation will therefore be a techno-economic feasibility study of the extraction process and subsequent metal production to ascertain its financial viability.

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