Hierarchization of Physicochemical Factors during Simultaneous Removal of Lead and Copper from the Marrakech Municipal Discharge Soils

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1.Introduction

Over the centuries, human activities have contaminated large areas in both developed and developing countries. An example of these areas is the city of Marrakech in the Kingdom of Morocco. The commercial and industrial activities of Marrakech promote the economy of the region but also generate many environmental problems. One of them is clearly the management of waste and residues from these different activities. The collection and burial activities of the Marrakech municipal waste dump play an essential role in the management of garbage in the province, but, on the other hand, they generate other problems, such as the management of soil, aquifer resources, and local flora and fauna contamination. Contaminants can be of two kinds: organic or inorganic. Organic contaminants, whose presence is mainly due to human activity, can be toxic and even carcinogenic [1]; they are issued from petroleum hydrocarbons, solvents, pesticides, etc. Inorganic contaminants are mainly metals (Cu, Fe, Ni, Zn, . . . ) and metalloids (As, B, Te, . . . ) found naturally in the Earth’s crust but the anthropogenic human activities cause these metals to accumulate on sites well beyond the concentrations inherited from the parent rock [2, 3]. Sometimes the concentrations are so high that they represent a danger to the fauna, flora, and human health. Heavy metals constitute a major factor of this pollution due to their atmospheric deposition, their leaching tendency, and the fact that they are nondegradable, unlike organic compounds. The cleanup usually requires their removal. Several decontamination techniques have been developed in research laboratories and industrial sites in order to eradicate this pollution or at least to minimize its effects. For example, we can cite electroplating [4], electrocoagulation [5], phytoremediation [6], extraction by adsorption [7], and extraction by organic complexing agents [8, 9].
Among the remediation techniques for soil contaminated with heavy metals, washing has given very interesting results. Various extraction agents have been used in the washing of soils such as acids, bases, surfactants, and complexing agents. Some of these extractants destroy the structure of the soil. Yobouet et al. reported that the use of HCl at pH = 0.5 dissolves all the nonresidual soil’s fractions and a part of the residual one [10]. This is not the case with complexing agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) which are powerful enough to efficiently extract the heavy metals retained in different fractions of the soil while preserving their consistency. Although less effective than EDTA, NTA is a more readily biodegradable reagent [11].

Two representatives of heavy metals were included in the study: Pb and Cu. The micronutrient Cu, called protective food, is necessary for life and represents only beyond a certain limit defined by the World Health Organization (WHO) among other institutions [12, 13]. On the other hand, Pb has no role in the physiological activity of animals or plants and constitutes a danger to human health [12, 14].

EDTA and NTA, Like a lot of other chelants, have already been studied for their extracting power of metals from the soil [9, 15, 16] and for their capability to increase the dissolution and availability of heavy metals during phytoremediation and soil wash [16, 17]. This extraction is determined by the physicochemical parameters of the soil-chelate system. Several parameters can influence the removal of heavy metals from the soil. We can mention pH, ligand, concentration, temperature, nature of the soil [18], etc. Our objective was to establish a hierarchy of physicochemical factors controlling the extraction efficiency of Cu and Pb from the soil of the municipal landfill of Marrakech by the use of two organic chelants, EDTA and NTA. We aimed also to study the interactions between these factors (synergistic or inhibitory) and finally to propose a modeling of this extraction according to factors. They are nature of the chelating agent [19], pH of the medium, the ratio mass of the soil to volume of the extractant solution [20], soil’s particle size [21], and the contact time between the soil and the extracting’s solution [18].

The experimental methodology was adopted to achieve these objectives: a fractional factorial design 2(5−1) was used to determine the effects of the five factors studied on the extraction and the intensity and the type of interactions between them [22].

2. Material and Methods

2.1. Samples Preparation. The soil studied consists of a mixture of several samples collected from depths up to 30 cm, from different locations in and around the Marrakech municipal landfill. Once dried in open air and under shade, the samples were sieved to 2 mm. After physicochemical characterization, they were separated into two fractions: the first one called fine and designated by (F) with particle diameter less than or equal to 1 mm, and the second called coarse and designated by (C) consisting of particles having a diameter between 1 and 2 mm. They were then stored in propylene jars until use.

2.2. Chemicals Preparation. The EDTA solutions were prepared from the ethylenediaminetetraacetate disodium salt delivered by Ferak GmbH Laboratory; for the NTA solution, the nitrilotriacetic acid, provided by Sigma Aldrich Company, was used. The solutions of the two ligands were prepared by dissolving the appropriate masses in bidistilled water. To promote the dissolution, a few crystals of sodium hydroxide have been added to increase the pH to alkaline value [23]. The solutions were then sealed and stored at 4°C until use. All reagents were of analytical grade.

2.3. Total Metal. To determine the metal content in the two classes of samples, acid digestion of 1.0 g of soil dry sample was carried out with a mixture of acids as follows [24, 25]:

(i) The sample was mixed with 2 ml of HClO₄ and 10 ml of HF and then heated to dryness.

(ii) Then, the precipitate was dissolved with 1 ml of HClO₄ and 10 ml of HF and heated until almost total evaporation of the liquids.

(iii) Finally, 1 ml of HClO₄ was added and the liquids were evaporated until white fumes appeared.

The solid was dissolved with 12N HCl and diluted to 25 mL. The solution was then stored in a tightly closed propylene jar and stored at 4°C until analyses, which were carried out by inductively coupled plasma atomic emission spectroscopy (AES-ICP).

2.4. Extraction. To extract heavy metals from soil samples, two ligands’ aqueous solution c = 0.01 mol L⁻¹ was used [9]: EDTA and NTA. The first is a relatively strong chelator [23, 26]; however it presents a risk of toxicity [23]. The second is biodegradable [27, 28] and has a structure similar to EDTA [29] and, therefore, a comparable chelating tendency. The value of the concentration was chosen taking into consideration two criteria: the ligand should be in excess of the different metal ions present in the medium, and according to the literature the optimal concentration is about 0.01 mol L⁻¹ [18, 23, 30, 31].

A mass m (1 or 5 g) of the fraction considered (F or C) was weighed and mixed with 20 mL of the solution, c = 0.01 mol L⁻¹, of the ligand (EDTA or NTA). The pH was adjusted to the desired value with molar solution of hydrochloric acid HCl and sodium hydroxide NaOH during stirring (240 rpm) time T (10 or 60 min), following the experimental design as shown in Table 1.

Once the time T has been consumed, the mixture was centrifuged at 2000 rpm for 10 minutes, and then the supernatant was filtered, acidified with a 10% nitric acid solution, and stored at the temperature of 4°C until its analysis by AES-ICP.
Table 1: Experimental design and the responses $Y_{Pb}$ and $Y_{Cu}$.

| No exp | Randomized order | Ligand | pH | m(g)/V (20 mL) | Size | Time (min) | Experimental design | Responses |
|--------|------------------|--------|----|----------------|------|------------|---------------------|-----------|
| 1      | 2                | EDTA   | 2  | 1              | F    | 60         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 39.231    |
| 2      | 3                | EDTA   | 2  | 1              | F    | 60         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 45.868    |
| 3      | 16               | NTA    | 2  | 1              | F    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 32.676    |
| 4      | 14               | NTA    | 2  | 1              | F    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 31.873    |
| 5      | 25               | EDTA   | 10 | 1              | F    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 17.485    |
| 6      | 17               | EDTA   | 10 | 1              | F    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 16.570    |
| 7      | 24               | NTA    | 10 | 1              | F    | 60         | X1 1 X2 -1 X3 -1 X4 -1 X5 1 | 2.518     |
| 8      | 13               | NTA    | 10 | 1              | F    | 60         | X1 1 X2 -1 X3 -1 X4 -1 X5 1 | 0.967     |
| 9      | 21               | EDTA   | 2  | 5              | F    | 10         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 40.941    |
| 10     | 9                | EDTA   | 2  | 5              | F    | 10         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 29.151    |
| 11     | 22               | NTA    | 2  | 5              | F    | 60         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 17.913    |
| 12     | 10               | NTA    | 2  | 5              | F    | 60         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 12.180    |
| 13     | 6                | EDTA   | 10 | 5              | F    | 60         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 9.115     |
| 14     | 19               | EDTA   | 10 | 5              | F    | 60         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 10.452    |
| 15     | 8                | NTA    | 10 | 5              | F    | 10         | X1 1 X2 1 X3 -1 X4 -1 X5 1 | 1.757     |
| 16     | 27               | EDTA   | 2  | 1              | C    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 1.327     |
| 17     | 7                | EDTA   | 2  | 1              | C    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 24.863    |
| 18     | 18               | EDTA   | 2  | 1              | C    | 10         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 39.012    |
| 19     | 4                | NTA    | 2  | 1              | C    | 60         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 29.990    |
| 20     | 26               | NTA    | 2  | 1              | C    | 60         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 33.547    |
| 21     | 30               | EDTA   | 10 | 1              | C    | 60         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 3.946     |
| 22     | 11               | EDTA   | 10 | 1              | C    | 60         | X1 -1 X2 -1 X3 -1 X4 -1 X5 1 | 4.459     |
| 23     | 1                | NTA    | 10 | 1              | C    | 10         | X1 1 X2 -1 X3 -1 X4 -1 X5 1 | 3.573     |
| 24     | 12               | NTA    | 10 | 1              | C    | 10         | X1 1 X2 -1 X3 -1 X4 -1 X5 1 | 3.573     |
| 25     | 15               | EDTA   | 2  | 5              | C    | 60         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 26.547    |
| 26     | 20               | EDTA   | 2  | 5              | C    | 60         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 24.685    |
| 27     | 23               | NTA    | 2  | 5              | C    | 10         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 14.125    |
| 28     | 5                | NTA    | 2  | 5              | C    | 10         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 15.810    |
| 29     | 28               | EDTA   | 10 | 5              | C    | 10         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 0.274     |
| 30     | 32               | EDTA   | 10 | 5              | C    | 10         | X1 -1 X2 1 X3 -1 X4 -1 X5 1 | 0.125     |
| 31     | 31               | NTA    | 10 | 5              | C    | 60         | X1 1 X2 1 X3 1 X4 1 X5 1 | 1.087     |
| 32     | 29               | NTA    | 10 | 5              | C    | 60         | X1 1 X2 1 X3 1 X4 1 X5 1 | 2.663     |

2.5. Factors’ Effects Measurement. The effect, on the efficiency of extraction, was investigated for the five factors [18, 32] (Table 2).

A two-level fractional factorial $2^{5-1}$ design [33, 34] was adopted to evaluate the effect of these factors on the extraction process and to estimate the interactions between them. Each factor was associated with a coded variable $X_i$ (centered and normalized) defined as follows [34].

$$X_i = \frac{U_i - ((U_{max} + U_{min})/2)}{((U_{max} - U_{min})/2)}$$ (1)

The goal was to determine the response’s coefficients of a first-degree model $Y_M$ (2) valid only for $X_i = +1$ and $X_i = -1$:

$$Y_M = b_0 + b_1 \times X_1 + b_2 \times X_2 + b_3 \times X_3 + b_4 \times X_4 + b_5 \times X_5 + b_{12} \times (X_1 \times X_2) + b_{13} \times (X_1 \times X_3) + b_{23} \times (X_2 \times X_3) + b_{14} \times (X_1 \times X_4) + b_{24} \times (X_2 \times X_4) + b_{34} \times (X_3 \times X_4) + b_{15} \times (X_1 \times X_5) + b_{25} \times (X_2 \times X_5) + b_{35} \times (X_3 \times X_5) + b_{45} \times (X_4 \times X_5),$$ (2)

where

(i) $M$ was the considered metal.

(ii) $Y_M$ was the efficiency of the metal’s extraction defined as follows:

$$Y_M (\%) = 100 \times \frac{C_{extract} (mg/kg)}{C_{metal\ total} (mg/kg)}$$ (3)

(iii) $C_{extract} (mg/kg)$ was the concentration of the metal in the extract.
(iv) $C_{\text{metal total}}$ (mg/kg) was the total concentration of the metal in the soil.

In addition, the other coefficients are described in Table 3.

Repetitions were performed to estimate accuracy and deviations. The $2^{5-1}$ factorial fractional experimental design, as generated by NEMRODW software, was reported in Table 1. The experiments were conducted in a randomized order; thus uncontrollable factors would not influence the results.

### 3. Results and Discussion

#### 3.1. Sample Characterization

The physicochemical properties of the samples are listed in Table 4.

The total metal content is shown in Table 5.

The samples were of slightly alkaline pH. The pH in the presence of KCl was slightly lower than that in water. This was explained by the displacement of acidic cations from the soil to the solution by the K$^+$ cations. In these conditions, the leaching of heavy metals by rainwater will be limited. The presence of organic matter suggested that the soil could potentially have a heavy metal retention property [37].

The total concentration of Pb was 53.8 ppm. It was beyond the RV (twice as large) without exceeding the VS.

For Cu the total concentration, 11.3 ppm, in the soil of the discharge was equal to the RV. As shown in Table 6, the total Cu content was the same in fraction F and C of the soil. Pb was more present in the fine fraction than in the coarse one. In order to determine the classification of the effects of factors on the extraction of metals from the soil, we preferred to work on samples with a low content of heavy metals. We thus hoped to increase the sensitivity of our tests. Thus, in future attempts at decontamination, we will probably act on the most determining factors for an optimal result.

#### 3.2. Metal Removal Study

The removal efficiency $Y_{\text{M}}$, as shown in Table 1, varied from 0.125% to 45% for Pb and from 1% to 85% for Cu depending on experimental conditions. The factors actually played a very important role. Indeed, the modification of the experimental conditions changed the extraction efficiency by a factor greater than 80 for both metals.

The coefficients as computed by NEMRODW software, based on the result of the 32 experiments of the experimental design, are given in Table 7 below with the corresponding $p$ factor (significance %).

Hence, the Pb extraction efficiency was expressed in (4) by the following.

\[
Y_{\text{Pb}} \text{ computed} = 16.82 + (-3.97) \times X_1 + (-11.83) \times X_2 + (-3.81) \times X_3 + (-2.55) \times X_4 + (-0.25) \times X_5 + 1.16 \times (X_1 \times X_2) + (-0.68) \times (X_1 \times X_3) + 2.17 \times (X_2 \times X_3) + 2.75 \times (X_1 \times X_4) + 0.02 \times (X_2 \times X_4) + 0.21 \times (X_3 \times X_4) + 0.01 \times (X_1 \times X_5) + (-0.34) \times (X_2 \times X_5) + 0.32 \times (X_3 \times X_5) + 1.85 \times (X_4 \times X_5).
\]

(4)

For Cu the efficiency of extraction was also given in (5) as follows.

\[
Y_{\text{Cu}} \text{ (computed)} = 34.94 + (-3.60) \times X_1 + (-24.15) \times X_2 + (-12.10) \times X_3 + (-0.34) \times X_4 + (-0.53) \times X_5 + 0.85 \times (X_1 \times X_2) + 0.29 \times (X_1 \times X_3) + 6.63 \times (X_2 \times X_3) + 1.68 \times (X_1 \times X_4) + (-2.27) \times (X_2 \times X_4) + (-3.08) \times (X_3 \times X_4) + 4.46 \times (X_1 \times X_5) + 0.09 \times (X_2 \times X_5) + (-0.19) \times (X_3 \times X_5) + (-0.13) \times (X_4 \times X_5).
\]

(5)

However, only the factors and interactions including the factor $p \leq 5\%$ are determining factors. They were indicated, in Table 7, by a *, **, or *** in the column giving the values of $p$.

#### 3.3. Factors Effect

The analysis of the results revealed that only pH ($b_2 = -24.15$), m/V ($b_2 = -12.1$), and ligand nature ($b_1 = -3.6$) were decisive factors for the extraction of Cu. For Pb extraction, the decisive factors were pH ($b_1 = -11.83$), ligand nature ($b_1 = -3.97$), m/V ($b_1 = -3.81$), and particle size ($b_4 = -2.55$). As expected pH was the most influential factor for both metals. Only Pb extraction was influenced by particle size. All the statistically significant effects have a negative coefficient: the decrease of those values increased the removal efficiency of the two metals from the soil.

3.4. The Interactions. We could not conclude on the effect of the different factors on the metals removal without taking into account the interactions between them. The different factors interacted positively or negatively and therefore determined the efficiency of the extraction. These interactions would favor the effect of factors when they are constructive (positive coefficient) or attenuate them when they are destructive (negative coefficient). Only the interactions between the significant factors were taken into account.

For Cu the pH/m/V ratio interaction was the only one to meet this requirement. They interacted positively ($b_{23} = 6.62$). As revealed in Figure 1, at pH = 10 the decrease of the ratio m/V increased the efficiency tree time but it remained low (16%). On the other hand at pH = 2, the variation was less important (two times) but the removal
efficiency reached 77.8%. The removal efficiency was maximal when pH and the ratio m/V were both at low level.

For Pb removal, the statistically significant interactions between factors were in decreasing order as shown in (Table 7): ligand/particle size ($b_{14} = 2.75$), pH/m/V ($b_{23} = 2.17$), and particle size/contact time ($b_{45} = 1.85$).

The other interactions were statistically insignificant: the $p$ factor was greater than 5%. The interaction between particle size and contact time ($b_{45}$) involved no significant factor (contact time). The most significant was that between ligand and soil particle's size ($b_{14} = 2.75$). As shown in Figure 2 the extraction efficiency, when using NTA as chelator, did not vary with particle size ($Y_{pb} = 13%$). However, with EDTA the Pb removal efficiency was better with particles of small size. The maximum ($Y_{pb} = 26%$) was reached when both factors were in their low level: EDTA as ligand and soil particle's size <1 mm.

In the second place came the interaction between the two factors pH and the ratio of soil mass to the volume of the chelator solution. As shown in Figure 3 the decrease of the ratio m/V increased the Pb removal amount. The variation was more important at pH = 2 than at pH = 10.

3.5. Effect of Ligand. The extraction with chelating agents aimed to measure the mobilizable metal fraction, that is to say, the active part of the pollution and a potentially active part that could be available depending on the physicochemical conditions. EDTA, like NTA, is a complexing agent strong enough to extract metals related to different soil's fractions (soluble, bound to carbonates, bound to oxide, and a part of the metal bound to organic matter) except the metal fraction bound to silica [38]. EDTA is a hexadentate chelating agent while NTA is tetradentate one. EDTA turned out to be better than NTA for the extraction of both metals ($b_{1} = -3.6$ for Cu and $-3.81$ for Pb). This was in agreement with the values of the formation constants of the considered chelates ($K_{f \text{CaEDTA}} = 20.6$, $K_{f \text{PbEDTA}} = 19.7$, $K_{f \text{CaNTA}} = 13.05$, and $K_{f \text{PbNTA}} = 11.4$) [39–41]. However, the extraction of Cu was not affected by the choice of the ligand ($b_{1} = -3.6$) which came in the third position relative to the pH ($b_{2} = -24.15$) and the m/V ratio ($b_{3} = -12.1$). On the contrary, the extraction of Pb depended on the nature of the ligand as shown in Figure 2. It was, like the ratio m/V, the second important factor after pH. This suggested that the efficiency of Cu extraction depends on the amount of ligand and the amount of Cu in soil solution. On the other hand, for

| Table 3: The $Y_i$ coefficients meaning [35]. |
|----|----|----|
| Coefficient | Name | Signification |
| $b_{0}$ | Constant | The average value |
| $b_{i}$ | Coefficient of $X_i$ | Linear effect of the associated factor |
| $b_{ij}$ | Interaction coefficient between $X_i$ and $X_j$ | Interaction between associated factors |

| Table 4: Physicochemical value summary. |
|----|----|----|----|
| pH (H$_2$O) | pH (KCl) | G (mS) | $r_{num}$ (%) | % mo |
| Max | 8.16 | 8.08 | 0.535 | 3.06 | 4.95 |
| Min | 7.6 | 7.12 | 0.502 | 2.77 | 3.87 |
| Average | 7.89 | 7.61 | 0.525 | 2.96 | 4.02 |

| Table 5: Metal total content and referential values. |
|----|----|----|
| Metal | Cu (mg/kg) | Pb (mg/kg) |
| Min | 11.80 | 43.96 |
| Max | 10.92 | 63.62 |
| Average | 11.36 | 53.79 |
| RV [36] | 14 | 25 |
| VS [36] | 50 | 200 |
| VI [36] | 145 | 400 |

For natural and agricultural soil, RV: reference value, an average natural value of metal concentration in soil as inherited from the mother rock; VS: threshold value, value of metal concentration beyond which studies must be conducted; VI: intervention value; if this value is exceeded, remediation measures must be taken.

| Table 6: Metal total content in F and C fractions. |
|----|----|----|
| MT mg/kg | Cu (mg/kg) | Pb (mg/kg) |
| C | 11.2 | 48.1 |
| F | 10.5 | 61.7 |

Given the above, we have adjusted the expression of the metal M removal efficiency $Y_M$ (computed) as $Y_M$ (adjusted) expressed in (6) and (7).

$$Y_{Cu} (\text{adjusted}) = 34.94 + (-3.60) \times X_1 + (-24.15) \times X_2 + (-12.0) \times X_3 + 6.62 \times (X_2 \times X_3).$$

(6)

$$Y_{Pb} (\text{adjusted}) = 16.82 + (-3.97) \times X_1 + (-11.83) \times X_2 + (-3.81) \times X_3 + (-2.55) \times X_4 + 2.17 \times (X_2 \times X_3) + 2.75 \times (X_1 \times X_4).$$

(7)

The two functions $Y_{Cu}$ (adjusted) and $Y_{Pb}$ (adjusted), although simplified, enabled us to find the values measured experimentally as shown by the two graphs $Y_{Cu}$ (adjusted) = $f(Y_{Cu}$ (experimental)) and $Y_{Pb}$ (adjusted) = $f(Y_{Pb}$, experimental)) in Figure 4. Correlation coefficients $R$ and standard deviation SD are given in Table 8.

Although simpler, both expressions contain all the information relating to the variation of the efficiency of extraction of the corresponding metal according to the different factors. Indeed the corresponding correlation coefficient, between the experimental removal efficiency and the calculated one, is 0.961 and 0.968, respectively, for Cu and Pb as shown in Table 8.
Pb, the metal-soil interaction and metal-ligand interaction were also decisive; there must be interference with the other constituents of the system. Labonowski et al [42] suggested that Cu had a more homogeneous binding strengths (with one or more soil constituents) compared to Pb. Cu was reported to be mainly retained in the organic and residual fraction of the soil and consequently it was strongly and uniformly bound to the soil. Dhe Pb was bound to different soil’s fractions and consequently it presented different behaviors according to the strength of its connection to the concerned fraction.

### 3.6. Effect of pH.

As expected, according to literature, pH was the most influential factor on the removal of both metals ($b_2 = -24.15$ for Cu and $-11.83$ for Pb) and the extraction efficiency was increased in acidic medium. This was in accord with the fact that the soil dissolution was promoted at low pH and hence the metallic ions became available in

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**Table 7: The $Y_{Cu}$ and $Y_{Pb}$ coefficients and their statistical significance.**

| Coefficients | $Y_{Cu}$ coefficients | $p$ factor (%) [1] | $Y_{Pb}$ coefficients | $p$ factor (%) [1] |
|--------------|----------------------|-------------------|----------------------|-------------------|
| b0           | 34.94                | $<0.01^{***}$     | 16.82                | $<0.01^{***}$     |
| b1           | -3.6                 | 1.23*             | -3.97                | $<0.01^{***}$     |
| b2           | -24.15               | $<0.01^{***}$     | -11.83               | $<0.01^{***}$     |
| b3           | -12.1                | $<0.01^{***}$     | -3.81                | $<0.01^{***}$     |
| b4           | -0.34                | 79.2              | -2.55                | 0.139**           |
| b5           | -0.53                | 68.8              | -0.25                | 71.1              |
| b12          | 0.85                 | 52.2              | 1.16                 | 9.3               |
| b13          | 0.29                 | 82                | -0.68                | 31.9              |
| b23          | 6.63                 | 0.0113***         | 2.17                 | 0.454**           |
| b14          | 1.68                 | 20.5              | 2.75                 | 0.0762***         |
| b24          | -2.27                | 9.2               | 0.02                 | 97                |
| b34          | -3.08                | 2.76*             | 0.21                 | 75.2              |
| b15          | 4.46                 | 0.311**           | 0.01                 | 98.7              |
| b25          | 0.09                 | 94                | -0.34                | 61.4              |
| b35          | -0.19                | 87.9              | 0.32                 | 63.8              |
| b45          | -0.13                | 91.6              | 1.85                 | 1.23*             |

1 Any parameter is statistically significant if the corresponding $p$ is less than or equal to 5%.
solution. An acidic pH leads to the dissolution of the metal salts, the dissolution of the retention phases, the cations’ desorption, and the anions’ adsorption. The solubility therefore decreases when the pH increases, goes through a minimum, and then increases when the element may exist in anionic form.

EDTA like NTA is polyacid. EDTA is a tetaacid ($pK_{a1} = 2$, $pK_{a2} = 2.7$, $pK_{a3} = 6.2$, and $pK_{a4} = 12.4$). For NTA ($pK_{a1} = 1.9$, $pK_{a2} = 2.5$, and $pK_{a3} = 9.7$). Because of the presence of a basic nitrogen atom in both ligands’ molecules, the sequestering tendency is strongly dependent on the pH value [39]. The chelator’s capacity decreased in acidic medium. Zhang et al [18] showed that EDTA free acid was more efficient for metal removal than its disodium salt. There had to be a compromise: the study suggested that the dissolution of the soil matrix was more decisive than the variation in the capacity of the chelator with pH. Indeed, F. Smith [43] reported that in the presence of metal the two ligands were mainly in the form of their respective complexes.

### Table 8: Correlation coefficient and standard deviation for $Y_M$ (adjusted) = $f(Y_M$ (experimental)).

| $Y_{Cu}$ (adjusted) | $Y_{Pb}$ (adjusted) |
|---------------------|---------------------|
| R = 0.961           | R = 0.968           |
| SD = 7.99           | SD = 3.53           |

3.7. Effect of Ratio m/V. This factor was the second important one after the pH for the removal of both metals. It is equal to the ratio of the mass of the soil by the volume of the ligand solution. The elimination efficiency was favored by a small ratio that signifies an excessive quantity of the ligand compared to the metal ions; thus, the extraction was more efficient.

This factor had a more preponderant effect on the extraction of Cu than on that of Pb ($b_3 = -12.1$ for Cu and $b_3 = -3.81$ for Pb). This difference could not be attributed only to the difference between the stability constants of the metal EDTA and metal NTA complexes ($K_f$CdEDTA = 20.6, $K_f$PbEDTA = 19.7, $K_f$CuNTA = 13.05, and $K_f$PbNTA = 11.4) [39–41]. For Cu, as suggested by Andrade [44], its extraction was not limited by the soil’s dissolution. The greater the quantity of ligand present, the greater the quantity of Cu extracted; this is the case when m/V is at its low level (m/V = 1/20). This was consistent with the fact that Cu is homogeneously retained in the soil [42]. But Pb’s extraction was limited by the soil retention and by the interference of other soil’s constituents [45]. The amount of Pb extracted was not only a function of the amount of ligand present; there had to be other factors involved. As we had already reported, Pb was bound to different soil’s fractions and consequently it showed different behaviors according to the strength of its connection to the concerned fraction. This could explain the difference in the effect of the factor m/V on the extraction efficiency of Cu and Pb.

3.8. Effect of Soil’s Particle Size. The smaller the particle size of the soil, the greater the specific surface presented to the ligand. Thus, the ligand metal interaction is more effective because the latter is more accessible. Consequently, the quantity of metal potentially accessible by the ligand will be greater [46]. Cu extraction was not significantly influenced by the soil’s particle size. This would suggest that the target portion of Cu was identically retained in the two fractions considered, F (for fine) and C (for coarse). Thus, the amount of Cu accessed by the ligand was controlled by the amount of ligand in solution (m/V factor) rather than by the soil’s metal retention process. Pb was better extracted from the fine fraction than from the coarse one [47]. This suggested that it was more present in fine fractions (size < 1 mm), as shown in Table 6 and proposed by many authors [46], and/or that it was more strongly retained in the coarse fraction (size > 1 mm). Pb ions would not be readily available to the ligand as explained when discussing m/V effect: the chelator, EDTA or NTA, had to compete with the bonding strength of Pb to the soil and probably to the other constituents of the soil, in particular, organic matter [48]. As we have seen in Table 6, Pb was more present in the fine fraction than in the large fraction of the soil, and therefore it was more extracted from fraction F than from fraction C. This could explain the effect of the size of the soil particles on the extraction of Pb. On the other hand, Cu was distributed identically over the two fractions F and C, and therefore the effect of the size factor of the soil particles was insignificant during the Cu extraction. In summary, the effect of particle size reflected the distribution of metals on the two fractions F and C.

3.9. Effect of Contact Time. Time was a statistically insignificant factor on the extraction of both metals. Increasing the contact time between the ligand solution and the soil...
from 10 to 60 minutes does not bring a significant gain in extraction efficiency. A 10-minute contact, while stirring at the speed of 240 rpm, between the soil and the ligand solution seemed sufficient to extract the two metals from the studied soil. During our preliminary tests, we worked with two contact durations of 1 and 10 hours. However, time was not a determining factor. We then chose to work with the two durations 10 and 60 minutes in the hope of having a significant contact time effect. This result did not mean that time had no effect on this extraction, but that its effect was much less significant than that of the four other factors studied. We suspected the existence of a competition between the phenomena of soil dissolution, metal complexation, and reprecipitation of the latter in other forms (carbonates, hydroxides, ...).

In summary, EDTA was a much more powerful chelator than NTA [42] as evidenced by the formation constants of the Cu and Pb complexes. The extraction of Pb by NTA was not affected by the particle size of the soil. However, the use of EDTA was sensitive to this factor. Being a powerful chelator, EDTA had access to fractions firmly linked to the soil. Consequently, the effect of the interface of the soil solution would be decisive: the smaller the size, the larger the interface and therefore the greater the amount of Pb extracted. Cu was a fairly mobile metal, so the quantity in solution would be decisive: the smaller the size, the larger the contact time, between the soil and the solution, was the least determining factor for the extraction efficiency of the two metals. The models represented by the two expressions $Y_{Cu}$ (adjusted) and $Y_{Pb}$ (adjusted) fairly well described the experimental results as indicated by the values of the correlation coefficients $R$ (0.961 for Cu and 0.968 for Pb). This comforted the choice of determining factors as being the statistically significant ones. An extraction efficiency of 45% was reached for Pb and 85% for Cu without optimization process.

### Data Availability
No data were used to support this study.

### Conflicts of Interest
The authors declare that they have no conflicts of interest.

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