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Evaluation of heavy metals in the soils of Karaikudi Town in India

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The Central Electro-Chemical Research Institute in India has a department that specializes in the design of both lead and nickel-chromium batteries. However, the laboratories activities have brought soils contamination of this department. This work involves assessing the presence of heavy metals such as lead, nickel and chromium in contaminated soils in the Center through the single and sequential extraction methods. Three samples were taken notably: the witness sample S1, which made it possible to determine the optimum parameters extraction (pH and concentrations of the extractant solutions) and then S2 and S3 which constitute the contaminated soils. Among the three extractants used for simple extraction (EDTA, $CaCl_2.2H_2O$ and CH_3COONH_4), the results show that EDTA extracts fairly high contents of Pb (77.63 ± 0.41 mg/kg), of Ni (67.37 ± 0.36 mg/kg) and Cr (60.22 ± 0.32 mg/kg). These contents constitute the bioavailable fraction of the three heavy metals and represent 69 to 84% of their total contents. The total contents contaminated soils are determined at 111.38 ± 0.59 mg/kg for lead, 79.95 ± 0.42 mg/kg for nickel and 74.47 ± 0.39 mg/kg for chromium. Compared with AFNOR standard NF U 44-041, the lead and nickel contents are higher. Moreover, the sequential extraction shows a large margin of the mobile and mobilizable fraction of all the metals studied in the contaminated soil samples. These results allow saying that there are risks of environmental pollution in the contaminated soils of the Central Electro-Chemical Research Institute.

Key words: Heavy metals, single extraction, sequential extraction, speciation, pollution.

INTRODUCTION

In the recent years, the development of human activities (metallurgical and chemical industries, agriculture, etc.) results in the accumulation of heavy metals in soils such as lead, nickel and chromium. These heavy metals are dangerous because of their toxicity to humans and their bioaccumulative nature (Muhammad et al., 2008; Jamali

et al., 2009). In fact, soil contamination poses a risk of toxicity to living things and humans through the food chain. It impedes the growth and viability of vegetation (Mpundu et al., 2013; Katoh et al., 2012). The heavy metals, namely chromium and nickel, are essential to the development of plants and animals. However, at

excessively high doses, they can be toxic. Others, such as lead, whose indispensability has not been shown, are potentially toxic (Alloway, 1995).

The geographic setting of this study is the Central Electro-Chemical Research Institute located in south India, Karaikudi town. It is a reference center in India that specializes in electrochemistry. A department of this Center, responsible for research on lead batteries and nickel-chromium batteries, has for several years carried out its research activities by dumping chemical effluents on soils. This practice led us to evaluate, in contaminated soils, the contents of three heavy metals concerned by this practice, in particular lead, nickel and chromium. However, unlike most organic contaminants, metallic elements are non-biodegradable and potentially toxic substances. Many chemical extraction (leaches) procedures have been proposed in the literature to estimate the mobility of metals in soil and sediments, or their bioavailability defined as the capacity of an element to be transferred from a soil fraction to a living organism, regardless of mechanism (Leleyter et al., 2012).

Indeed, the work carried out in the framework of this study, are much more oriented toward simple extraction while also addressing the sequential extraction to highlight the mobile and mobilizable fraction (or "labile") of metals in the soils studied. The reason for this choice is that simple extractions performed in one step, are inexpensive and fast (Leleyter et al., 2005). The advantage of the sequential extractions protocols resides in the use of appropriate chemical reagents to release various fractions of heavy metals from the soil. Each extraction is supposed to destroy the binding agent between the metal and the solid fraction of soil, allowing the metal species to be detected by appropriate analytical procedures. For this study, the compounds used for the simple extraction are the complexing EDTA and the salts $CaCl_2.2H_2O$ and CH_3COONH_4. The extraction with the solutions of $CaCl_2.2H_2O$ and CH_3COONH_4 aims at quantifying the active part of the pollution (mobile fraction) and best represents the intrinsic conditions of the soil in terms of ionic strength. EDTA extraction aims to measure the mobilizable metal fraction, that is to say the active part of the pollution and a potentially active part. Indeed, EDTA is a chelating agent with an ability to extract metals present in non-silica-bound phases, including metals complexed with organic ligands (Garrabrants et al., 2000). For extraction with EDTA and the salts $CaCl_2.2H_2O$ and CH_3COONH_4, a study was carried out with the witness soil (Uncontaminated soil of Center) in order to determine the optimum pH and the optimal concentration of the extractant solutions in order to reach better the extractable maximum.

All metallic elements present in the soil or sediment are potentially mobilizable if changing from a physicochemical parameter such as pH, the redox-potential and/or concentration of ligands (Katoh et al., 2012). Among the factors that have the greatest impact on the mobility of metals is pH. The pH of the medium influences the solubility of metals by altering the balance of distribution of metals between the liquid phase and solid phase (Leleyter and Baraud, 2005). When the elements are stable in cationic form (Pb^{2+}, Cr^{3+} or Cr^{6+}, Ni^{2+}, etc.), the increase of pH promotes the deprotonation of the soil particles and thus increases the binding of cations by the soil. For this reason, the extraction was carried out in an acid medium to promote the solubility of the metal cations.

To effectively remediate heavy-metal-contaminated soil, it is necessary to know the amount of toxic elements in the soil (Katoh et al., 2012). The objective of this work is to evaluate the contents of heavy metals in contaminated soils of the Central Electro-Chemical Research Institute using simple and sequential extraction methods in order to locate the potentially mobilizable fraction.

MATERIALS AND METHODS

Sampling

All experiments (Extraction of heavy metals) were carried out on three types of soil (S1, S2 and S3). These three soil samples were collected at Central Electro Chemical Research Institute in India. The contaminated soils (S2 and S3) were collected from depths of 0–15 cm. The sampling covers all "fine earth" of study zone (The size less than 2 mm). The first soil sample (S1) was used to search the optimum extraction parameters. The soil S1, which is remote from the sampling zone of the samples S2 and S3, has never received any products nor chemical effluents before. However, on soils where samples S2 and S3 are collected, are dumped for many years, the chemical effluents of laboratories containing heavy metals (Pb, Ni and Cr). The soils S2 and S3 are collected on two different sites in Central Electro Chemical Research Institute. S2 was collected on the floor where the laboratory of lead battery is located and S3 on the floor where the laboratory of nickel and chromium battery is located.

To better appreciate the percentage of extraction of metals, the soil sample S1 was artificially contaminated with lead on the one hand and, on the other hand, with nickel and chromium. Three samples were reconstituted with S1.

i) The sample $S1_0$ is the soil sample S1 which has not undergone any artificial addition of heavy metals and is considered like a witness sample for $S1_1$ and $S1_2$,
ii) The $S1_1$ sample is the soil sample S1 which has been artificially contaminated with lead, and
iii) The $S1_2$ sample is the soil sample S1 which has been artificially contaminated with nickel and chromium.

All soil samples S1, S2 and S3 were dried in the open air for 48 h and then passed in an oven at 50°C until complete drying. They were then ground and sieved with a sieve of 63 µ to obtain a very fine powder.

Preparation of solutions

Artificial soil contamination S1 was made by mixing 1% of product and 99% of soil, in terms of mass. The addition of lead, nickel and chromium was made by mixing S1 with aqueous solutions of lead

acetate (Sample $S1_1$), nickel chloride and potassium dichromate (Sample $S1_2$). Three extractant solutions were prepared: l'ethylenediaminetetra aceticacide (EDTA), Ammonium acetate pure (CH_3COONH_4) and the Calcium chloride dihydrate ($CaCl_2.2H_2O$). The optimal extraction concentration is determined by preparing for each extractant solution three different concentrations (0.1, 0.2 and 0.3 mol/L). These three concentrations constitute the best extraction concentrations after a series of extraction between 0.05 and 1 mol/L.

Total heavy metals

The total content of heavy metals of the soil samples S1, S2 and S3 was determined by acid attack to aqua regia (1/3 ; HNO_3/HCl).

Single extraction

The extraction of heavy metals was made using the ratio solid/liquid 1:10 (Leleyter et al., 2012). The extractant solutions were adjusted to pH 2, 3 and 4 with pure nitric acid. This is carried out by mixing 50 ml of the complexing solution with 5 g of soil sample under continued magnetic stirring for 2 h at room temperature.

The mixture was then centrifuged at 4000 rev/min for 15 min and filtered through filter porosity 0.45 µm and then stored at 4°C. The extracts were assayed by AAS (Atomic Absorption Spectroscopy). The optimum parameters (pH and concentration) of extraction of heavy metals found with S1 were applied to the soil samples S2 and S3 to determine their state of contamination.

Sequential extraction

The application of the procedure of BCR (The community Bureau of Reference) aims to allocate each pollutant according to three fractions (to which one can add a fourth unextracted called residual fraction) which are characteristic of the mode and the fixing intensity of each pollutant on the compartments of the soil (Ure et al., 1993). Sequential extraction was used only on the soil samples S2 and S3. In sequential BCR extraction, the soils samples are treated with a chain of reagents and determined the elemental concentration into fractions, linked with different mineralogical phases (Quevauviller, 2002). The different fractions of the sequential extraction are: The exchangeable and acid-soluble fraction (F1); the reducible fraction (F2); the oxidizable fraction (F3) and the residual fraction (F4). Scheme 1 shows the different steps of the extraction.

RESULTS AND DISCUSSION

Optimization of the concentration extraction

In the literature, some heavy metals are extracted by EDTA at a concentration of 0.05 mol/L (Leleyter et al., 2012). For this work, metals were extracted with the extractant solutions at different concentrations and by varying the pH in order to optimize the target parameters. The optimization was done with three extractant solutions at different concentrations (0.1, 0.2 and 0.3 mol/L). The extraction pH is that of the extraction solution while the single extraction was made with samples $S1_1$ and $S1_2$. The choice of compounds lead nitrate, nickel chloride and potassium dichromate for artificially polluted S1 is justified by the fact that they are more soluble in aqueous solution

(Lide, 1992). Three tests were needed for each concentration. The following figures show the extraction results.

The results show a better extraction of lead and nickel with EDTA at a concentration of 0.3 mol/L (Figures 1 and 2). However, the extraction of chromium by EDTA is important at a concentration of 0.1 mol/L (Figure 3). These results are in agreement with those of Jean (2007), which found a maximum concentration of 0.1 mol/L of EDTA necessary for a better extraction of Cr. This agent (EDTA) is also used in the determination of bioavailable fraction in soil (Grygo-Szymanko et al., 2015).

Calcium chloride ($CaCl_2.2H_2O$) has an significant extraction at 0.1 mol/L for the three metals (Pb, Ni and Cr). These results are consistent with those of Lebourg et al. (1996) who has shown that, for a better extraction of heavy metals, the maximum concentration of $CaCl_2.2H_2O$ is 0.1 mol/L and allows a good evaluation of the bioavailability of heavy metals in soils. Ammonium acetate (CH_3COONH_4) meanwhile better extracts the lead with a concentration of 0.1 mol/L. The contents of Ni and Cr are more important with ammonium acetate at a concentration of 0.3 mol/L.

The total contents of the three heavy metals in $S1_1$ and $S1_2$ are respectively 990.60 ± 5.24 mg/kg for lead, 208.42 ± 1.10 mg/kg nickel and 185.68 ± 0.98 mg/kg for chromium. The total contents allowed calculating the extraction percentages of the three components by extractants presented in Table 1.

This percentage is calculated with the best contents (Contents of the optimal concentrations) of the heavy metals of previous extractions (Figures 1, 2 and 3) using the following formula:

$$\%\text{Extract element} = \left(\frac{Metal\ extrated\ by\ Single\ extraction}{Metal\ extrated\ by\ acid\ mineralisation} \right) \times 100 \qquad (1)$$

Through these results (Table 1) we notice that, EDTA extracts better the three heavy metals while compared to the other extractants. This confirms the results of the literature that, EDTA is recognized as a powerful reducing agent and complexing (Forstner, 1993; Finžgar et al., 2007). The EDTA is a powerful complexing which forms with the metal species, the stable and soluble compounds. However, chromium is less extracted with EDTA compared to other metals. This is due to the low affinity of EDTA for the Cr compared to other extractants. Other works have shown that the citric acid has a greater affinity for Cr (Jean, 2007).

Optimization of the pH extraction

The solubility of heavy metals often depends on the variation of certain parameters such as pH (Leleyter and Baraud, 2005). The pH is a very important parameter in
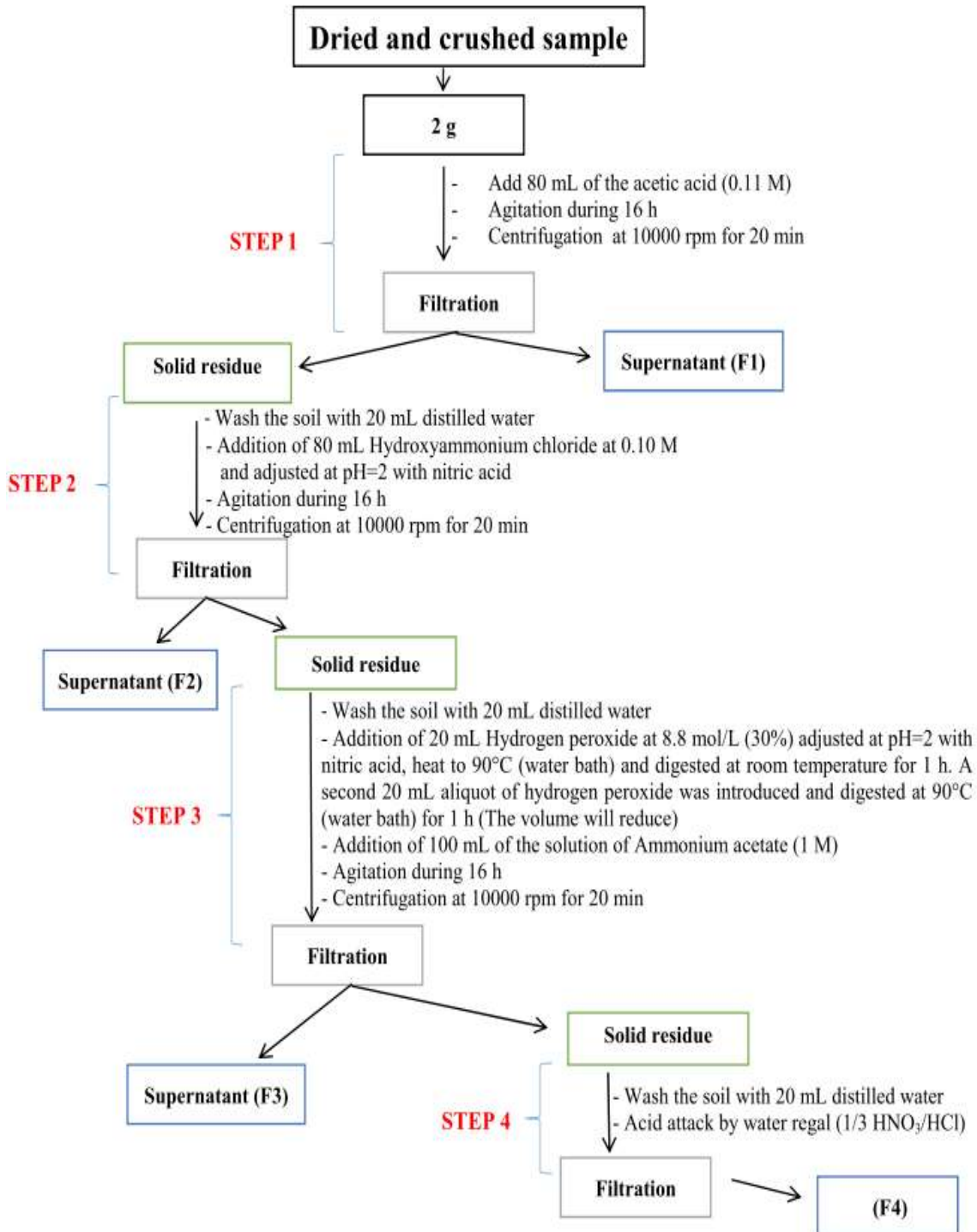
Scheme 1. Different steps of the sequential extraction.

the case of the solubilization process, particularly in the case of heavy metals.

The elements are all the more soluble as the pH decreases. At pH values above 6, the solubilized amounts are very small compared to the total content. Indeed, the optimization is done by varying the pH to 2, 3 and 4 of the extract solution with the optimal concentrations obtained. The pH is adjusted with nitric acid. This optimization allowed to examine the influence of pH on the release and the solubility of species present in the soil. The following figures show the extraction of heavy metals at various pH values with the optimal contractions extractants.
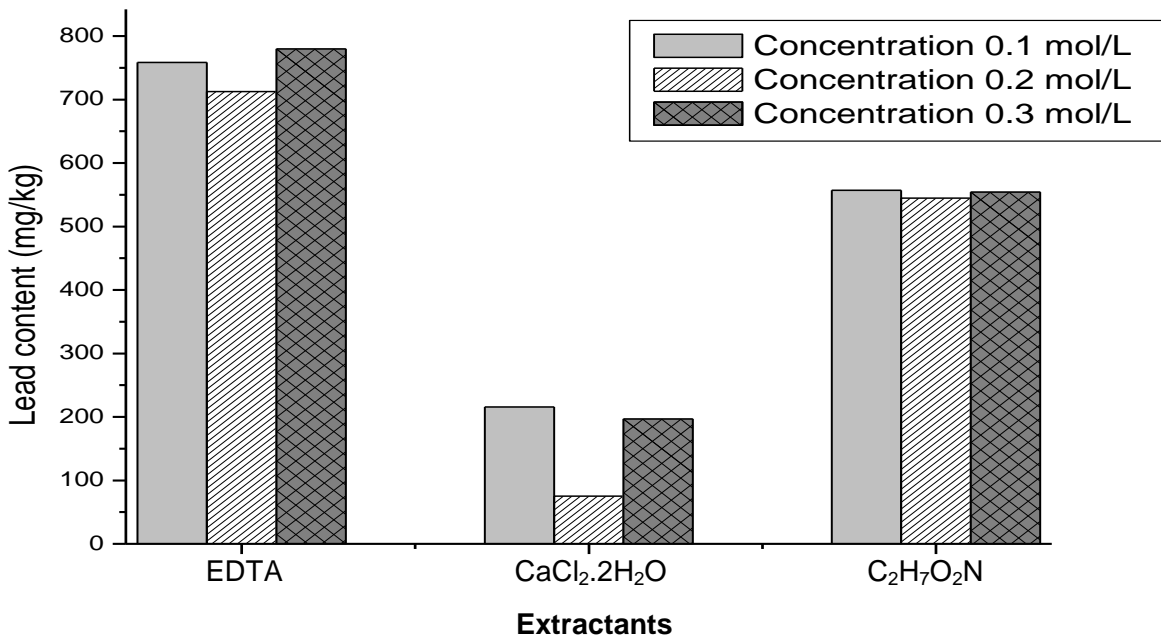
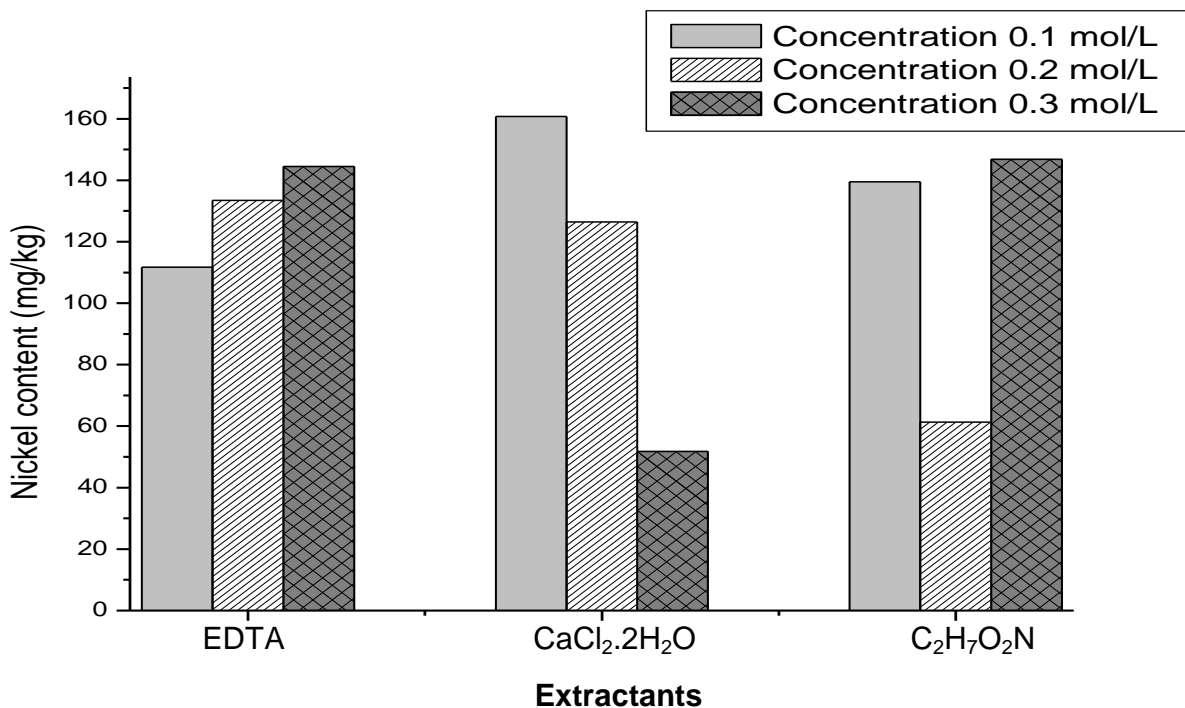**Figure 1.** Single extraction of lead at the different concentrations.

Figure 2. Single extraction of nickel at the different concentrations.

The results show that at a concentration of 0.3 mol/L EDTA, lead and nickel are more extracted at pH 4 (Figures 4 and 5). This is consistent with the results obtained by Oudghiri et al. (2011). On the contrary, at the same concentration of EDTA, chrome is more extracted at pH 2. The pH optimum extraction of $CaCl_2.2H_2O$ for the three metals is the same (pH 2) (Figures 4, 5 and 6). The Ammonium acetate extracts more lead at pH 2, the
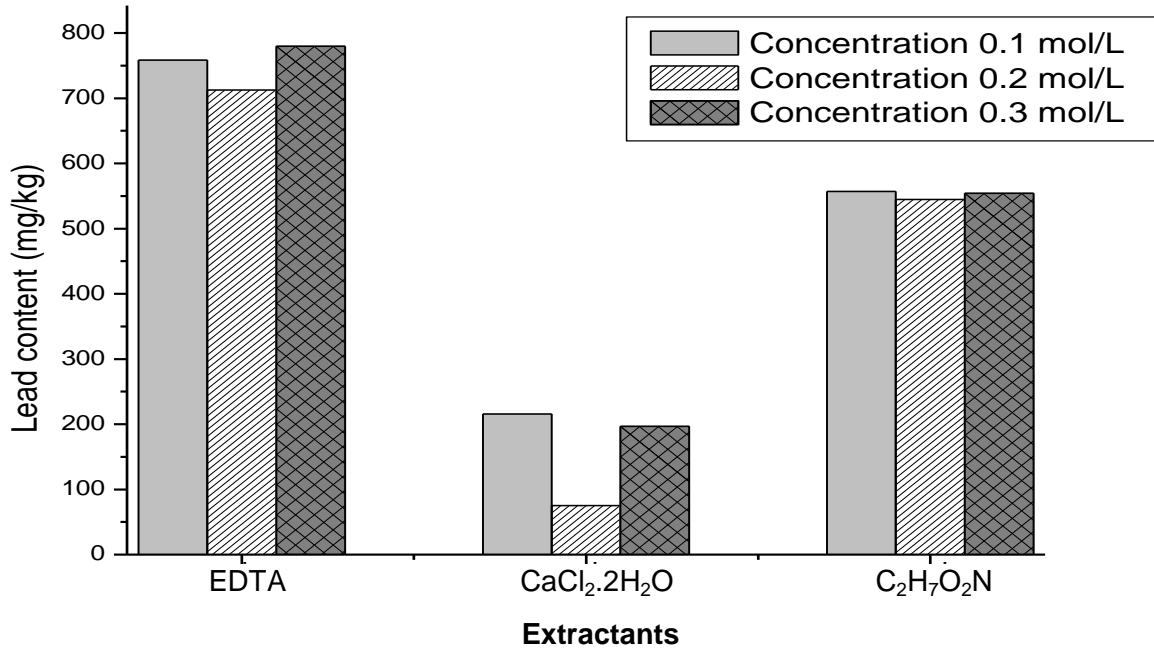
Figure 3. Single extraction of chromium at the different concentrations.
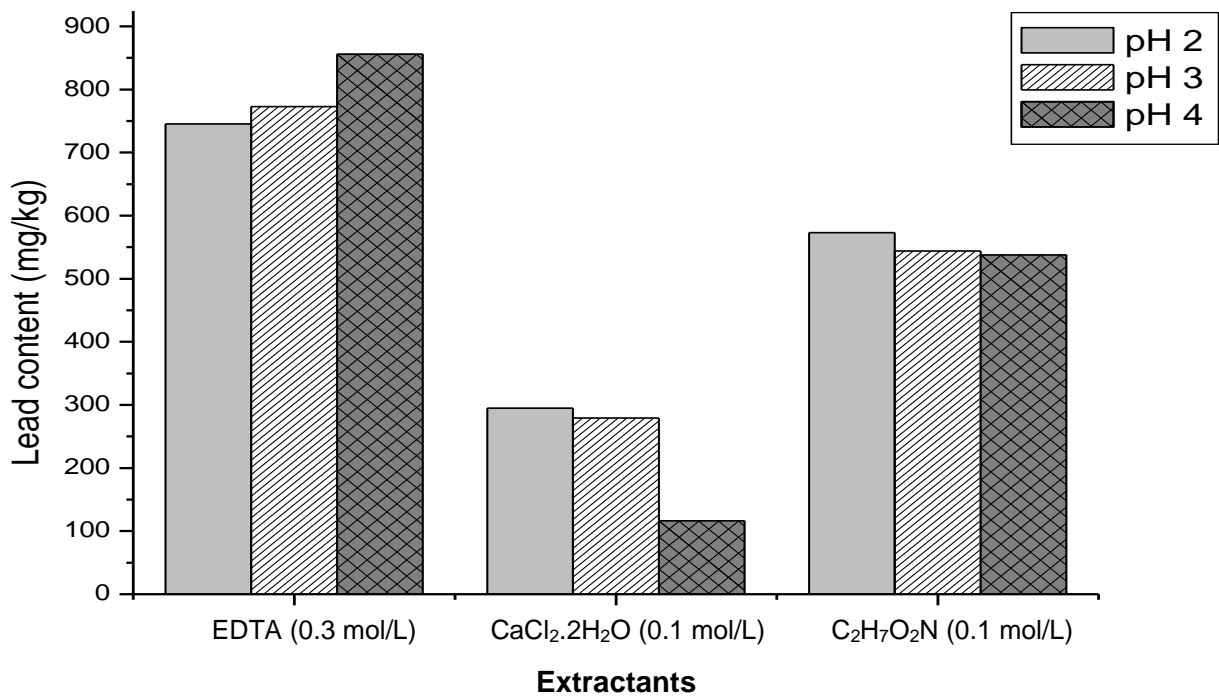

Figure 4. Single extraction of lead at different pH.

nickel and chromium at pH 4. For Mpundu et al. (2013), most metallic elements are mobile in the soil solution at pH <6. The optimum pH is important in the extraction of metals because it is a major factor in the retention of the metals and it controls all the processes affecting the behavior of these elements (Bourg, 1998). The chemical sensitivity of the materials as a function of pH is an important parameter for determining the solubilization of
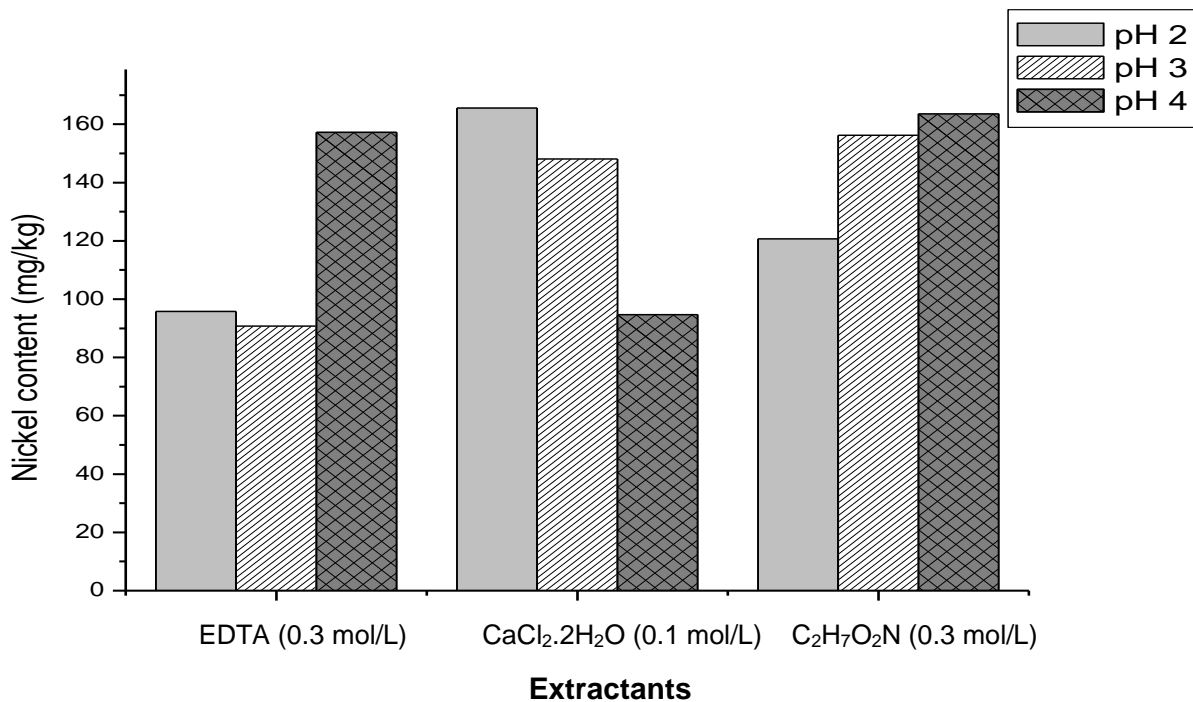
Figure 5. Single extraction of nickel at different pH.
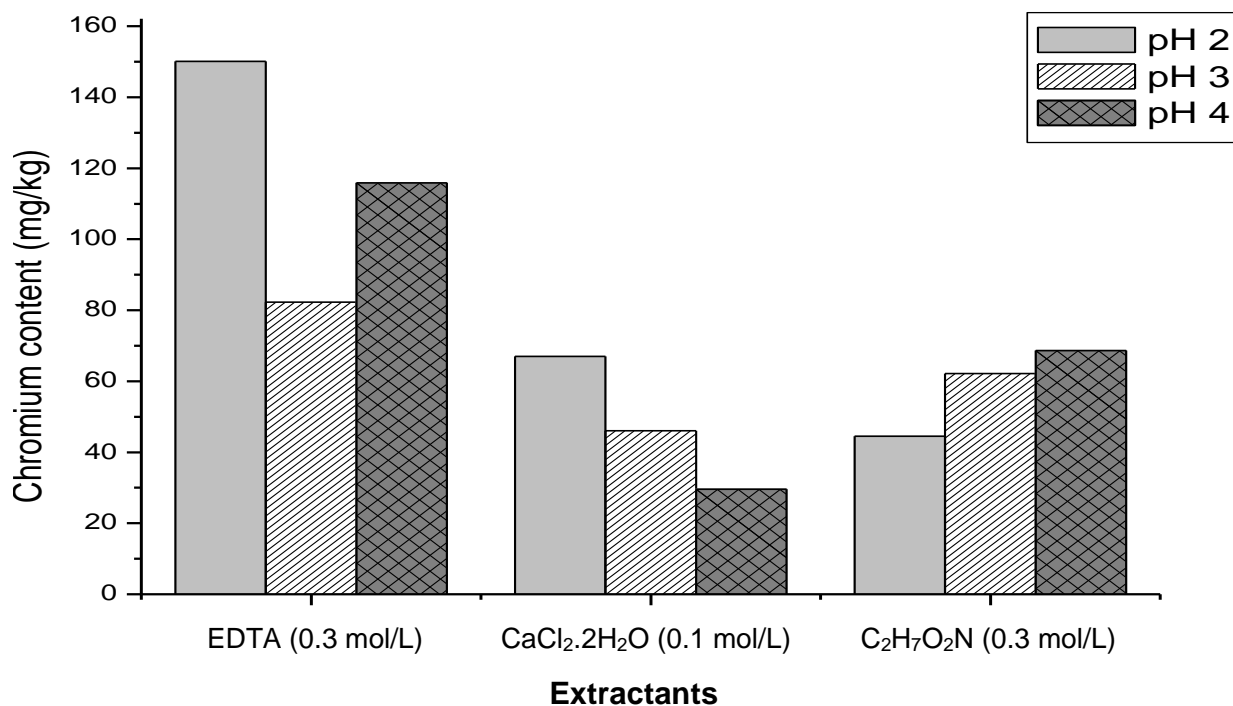

Figure 6. Single extraction of chromium at different pH.

pollutants. The more the pH decreases, the more the elements are soluble (Matera and Hecho, 2001).

The percentage extraction of heavy metals with different extractants and pH varying is calculated in the same way

Table 1. Extraction percentage of heavy metals with different extractants.

Heavy metals	%Pb	%Ni	%Cr
EDTA	75.73	62.33	54.04
$CaCl_2.H_2O$	16.4	54.21	27.78
$C_2H_7O_2N$	55.71	55.59	25.87

Table 2. Extraction percentage of heavy metals with different extractants with the optimal pH.

Heavy metals	%Pb	%Ni	%Cr
EDTA	79.88	54.99	62.54
$CaCl_2.H_2O$	23.23	65.3	25.6
$C_2H_7O_2N$	55.68	70.43	31.48

Table 3. pH and concentrations optimal of heavy metals.

Heavy metals	Concentration (mol/L)/pH		
	Pb	Ni	Cr
EDTA	0.3 / 4	0.3 / 4	0.1 / 2
$CaCl_2.H_2O$	0.1 / 2	0.1 / 2	0.1 / 2
$C_2H_7O_2N$	0.1 / 2	0.3 / 4	0.3 / 4

Table 4. Extraction of metals in the soil S1 with EDTA (0.05 mol/L).

Metal (mg/kg)	pH 2	pH 3	pH 4
Pb	663.54	502.68	588.18
Cr	29.97	11.84	8.88
Ni	179.50	39.30	24.00

as before (Table 1). It is especially significant for EDTA than for other extractants. However, the percentage of extraction of lead by EDTA is almost the same as that found by Lydia (Leleyter et al., 2005). The $CaCl_2.2H_2O$ salt appears less aggressive for Pb and Cr as compared to other extractants (Table 2).

Recapitulation of optimizations settings

Table 3 shows the optimum extraction parameters of the three heavy metals. It is found that the optimal concentrations of extractants are not the same for all three heavy metals. Similarly, the optimum pH for maximum solubility of the metal is not the same (Table 3). In order to compare the results with those of the literature, extraction was carried out with EDTA at a concentration of 0.05 mol/L (Katoh et al., 2012). Table 4 shows the contractions in mg/kg of extraction with EDTA

(0.05 mol/L) of metals in the soil S1.

Besides nickel extraction at pH 2, all other concentrations (Table 4) are lower than those found with EDTA at concentrations of 0.1, 0.2 and 0.3 mol/L (Figures 4, 5 and 6). These results are not in agreement with some of the literature that says, the optimum concentration of EDTA extraction is 0.05 mol/L. It is noted that most of the results of the literature did not take into account the influence of pH in the extraction of metals. In contrast, for Segues et al. (2004), for highly polluted soils, it is necessary to work with EDTA concentration to 0.3 mol/L but in basic medium.

Application of the optimum parameters

Single extraction

The single extraction of heavy metals with salts

Table 5. Single extraction of metals with the optimal settings of samples S2 and S3.

Heavy metals	Pb		Ni		Cr	
	mg/kg	%	mg/kg	%	mg/kg	%
EDTA	77.63 ± 0.41	69.7	67.37 ± 0.36	84.27	60.22 ± 0.32	80.86
CaCl$_2$.2H$_2$O	41.94 ± 0.22	37.65	46.25 ± 0.24	57.85	36.00 ± 0.20	48.34
C$_2$H$_7$O$_2$N	52.27 ± 0.28	46.93	56.01 ± 0.30	70.06	40.92 ± 0.22	54.95

(CaCl$_2$.2HO$_2$; CH$_3$COONH$_4$) allows quantifying the active part of pollution (mobile fraction) and to best represent the intrinsic soil conditions in terms of ionic strength. This simple extraction with EDTA complexing allows better measurement of the mobilized metal fraction and a potentially active part. Indeed, EDTA is a chelating agent having an extractability capacity of metals present in unbound to silica phases, including metals complexed with organic ligands.

The optimum parameters found with the S1 soil samples were applied to soil samples S2 and S3 for the single extraction. Three trials were needed for each soil sample. The total contents of the three metals were also determined by hot acid attack. The total contents in the samples S2 and S3 are respectively 111.38 ± 0.59 mg/kg for lead (Sample S2), 79.95 ± 0.42 mg/kg for nickel and 74.47 ± 0.39 mg/kg for chromium (Sample S3). Compared with AFNOR standard NF U 44-041 (100 mg/kg for lead, 50 mg/kg for nickel and 150 mg/kg for chromium), the lead and nickel contents are higher. The extraction percentages of metals in the Table 1 were calculated on the basis of the total contents.

The rate of extraction of metals using various extractants is high with a maximum of 84.27% of nickel extraction with EDTA and a minimum of 37.65% extraction of lead by CaCl$_2$.2H$_2$O (Table 5). The competition phenomena between the elements with the complexing can then take place, thereby limiting the mobilization of Cr and Ni. The treatment of heavy metal contaminated soil specifically Pb, Ni and Cr by three extractants (EDTA, CaCl$_2$.2H$_2$O and CH$_3$COONH$_4$) would give a better result with the optimization settings application. The extracted contents are much more related to the pollutants solubilization capacity by extractants. As far as the pollution of soils is concerned, we note with regard to the maximum permissible concentrations as defined by CCME 1999 (Vandana et al., 2011) (70 mg/kg for Pb, 50 mg/kg for Ni and 64 mg/kg for Cr) that the total contents of Pb and Ni are higher. It shows a pollution of these two elements in the soils S2 and S3.

The total contents in S1$_0$ (Witness Sample) are 15.37 ± 0.08 mg/kg for Pb, 8.35 ± 0.04 mg/kg for Ni and undetected for Cr. The low levels recorded in the witness soils show the significant presence of heavy metals in soil S2 and S3 caused by the rejection of chemical influents. The use of extractants such as EDTA and CaCl$_2$.2H$_2$O

allowed highlighting respectively the mobilizable fraction and the movable portion of the soil matrix. This extraction shows that the proportion of the mobilizable fraction of the soils S2 and S3 is between 37 and 84% (Table 5). These proportions are high compared to the work of Kebir (2012).

Sequential extraction

The sequential extraction was performed on the samples S2 and S3 (Pb in S2, Ni and Cr in S3) to estimate the importance of the mobilized fraction (or "labile") of metals in the soils studied. The sequential extraction used comprises four fractions according to BCR:

i) The exchangeable and acid soluble fraction (F1), extracted by the acetic acid solution contain the heavy metals that are easily mobilizable.
ii) The reducible fraction (F2), extracted by the solution of hydrochlorure of hydroxylamine contains metals bound to the oxides that can be also mobilizable.
iii) The oxidizable fraction (F3), extracted with the peroxide of hydrogen and the solution of ammonium acetate contains metals bound to the organic matter, which can be released under oxidising conditions.
iv) The residual fraction (F4).

All metals studied are found in the four retention functions listed in the Protocol to BCR (Figure 7). It is noted that the exchangeable and acid-soluble fraction (F1) of the three metals is greater and exceeds 50%. This exchangeable and acid soluble fractions extracted by the acetic acid solution contain the heavy metals that are easily mobilizable. This result for the nickel does not comply with certain works of literature which state that the nickel is preferentially absorbed by the clays, the oxides of iron and manganese and can substitute for manganese in clay minerals of the soil. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils (McLean and Bledsoe, 1992).

The reducible fraction (F2) extracted by the solution of hydrochlorure of hydroxylamine contains metals bound to the oxides that can be also mobilizable. It represents the second most important fraction extracted for the three metals (between 21 and 38%) (Figure 7). These results
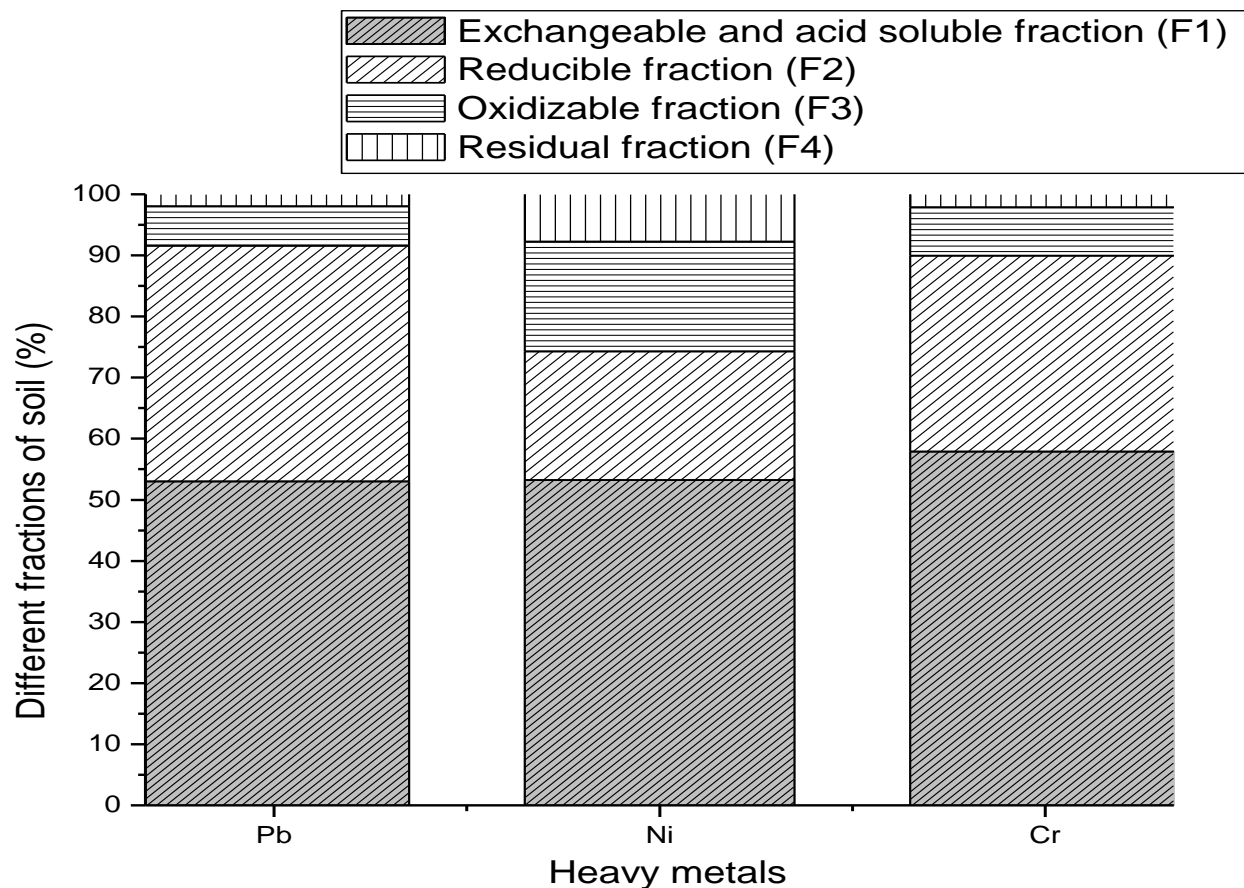
Figure 7. Heavy metals distribution in the different fractions of the samples S2 (Pb) and S3 (Ni and Cr).

are not consistent with those of Katoh et al. (2012), who demonstrated that the fraction bound to oxide is higher particularly for lead. The oxidizable fraction (F3) extracted with the peroxide of hydrogen and the solution of ammonium acetate contains metals bound to the organic matter. It is present at a low rate compared to the previous two fractions. The residual fraction (F4) is gotten after acidic attack of the residue of the oxidizable fraction. This fraction extracted is estimated between 1 and 7% (Figure 7). Its strong proportion in the residual fraction will entail a weak mobility of this element in the samples because, the residual fraction contains the metals that are little likely to be loosened in the normal environmental conditions (Bodjona et al., 2012; Leleyter et al., 1999). The metals present in the matrix of soil, often behave differently according to their position in the different fractions. In some compartments of soils like the example of the oxidizable fractions (F3) and residual (F4), metals are bound solidly, which makes their solubilization difficult. On the other hand, in other exchangeable, acid soluble fractions (F1) and reducible fraction (F2), metals are weakly absorbed and can be easily mobilized. However, we quantified the portion of metals contained in the F1 and F2 fractions in order to estimate the risks of

the immediate pollution. This portion is 91.58% for lead, 74.27% for nickel and 89.93% for chromium. Besides, those heavy metals have very elevated pollution risks in the studied soils. These results confirm the proportion of the mobilizable fraction recovered with the use of EDTA as an extractant (Table 5). However, only a few studies have compared the amount of heavy metal extracted with EDTA and the amount of sequential extraction (Cid et al., 2002).

A check on the results of BCR sequential extraction procedure was performed by comparing the sum of the four fractions (F1, F2, F3 and F4) with the total concentrations of heavy metal from digestion procedure. The detailed calculations were expressed as follows:

$$\%Recovery = (\frac{F1+F2+F3+F4}{Total\ concentration}) \times 100 \qquad (2)$$

This estimation approach of the percentage of recovery of the studied elements will enable a judgment on the effectiveness of extractants used and the margin of error made during the extraction of these metals. The protocol used allowed to extract more than 68% of metals from their total fraction (Table 6).

Table 6. Percentage recovery of heavy metals.

Metal	Total Concentration (mg/kg)	F1 + F2 +F3 +F4 (mg/kg)	%Recovery
Pb	111.38	93.29	83.76
Ni	79.95	69.58	87.02
Cr	74.47	50.84	68.27

Conclusion

Few works bring out the pH in the extraction of heavy metals. This work has led not only to find the optimal extraction concentration of lead, nickel and chromium but also the optimum extraction pH. The application of these optimum parameters on the contaminated soils samples of Central Electro-Chemical Research Institute, allowed to extract an important amount of heavy metals with a maximum of 84.27% of the total content.

However, the extractant $CaCl_2.2H_2O$ is less aggressive in the extraction of metals. On the other hand, EDTA turns out to be a good agent extractant with a rate of up to 79%. The sequential extraction shows a significant proportion of potentially mobilizable fraction of metals in the soil matrix. Through these results, it appears that, the recovery percentage is higher in the sequential extraction method than in the simple extraction method.

Compared with AFNOR standard NF U 44-041, the lead and nickel contents are higher in the soils studied. The high proportion of the mobilizable fraction of heavy metals in contaminated soils, prove the risk of pollution of this soils.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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