SEGUENTIAL EXTRACTION OF LEAD , NICKEL AND CADMIUM ELEMENTS IN CONTAMINTED SOILS

Ahmed Kareem Abbas*
Collage of Agriculture
University of AL-Qasim Green

Dr.Hamid Hussein R. Al-Jubouri
Collage of Agriculture
University of Baghdad

ahmedkareemabbas@yahoo.com

ABSTRACT

The study included samples were taken from soil by two Depth (30, 60 cm), with Silty Loam texture, from five locations close to the Euphrates plant for chemical materials and Al Sadda cement in Babylon Province to study the soil contamination with heavy elements (lead, nickel and cadmium) and their presence in the soil through successive extraction. The results showed that the soil components differ in the ability to reserve a quantity of heavy elements and this depends on the proportion and type of that component in the soil. The sequence of soil components was in the retention of heavy metals based on concentration (carbonate minerals< iron oxides and hydroxides< clay< organic substances) the sequence of heavy elements in each component of soil (lead <cadmium< nickel).

Keywords: Contaminated soil, Sequential Extraction, Lead, Nickel, and Cadmium.

*Research paper from the thesis of PhD for the first Author

الاستخلاص المتعاقب لعناصر الرصاص والنيكل والكادميوم في ترب ملوثة

أحمد كريم عباس*
كلية الزراعة / جامعة القاسم الخضراء

د.حامد حسين رجب الجبوري
كلية الزراعة / جامعة بغداد

ahmedkareemabbas@yahoo.com

الملخص

تضمنت الدراسة أخذ عينات تربة ذات نسجة Silty Loam بعمقين 30 و 60 سم من خمسة مواقع قريبة من معملي الفرات للمواد الكيميائية وأسمنت السدة في محافظة بابل وذلك لدراسة تلوث التربة بالعناصر الثقيلة (الرصاص والنيكل والكادميوم) وصور تواجدها في التربة وذلك بإجراء الإستخلاص المتعاقب ، وأظهرت النتائج أن مكونات التربة تختلف في قابلية حجز كمية من العناصر الثقيلة وهذا يعتمد على نسبة ونوع ذلك المكون في التربة ، وكان تسلسل مكونات التربة في حجز العناصر الثقيلة إعتماداً على التركيز (معادن الكاربونات < أكاسيد وهيدروكسيدات الحديد < الطين < المادة العضوية) أما تسلسل العناصر الثقيلة في كل مكون من مكونات التربة (الرصاص < الكادميوم < النيكل) .

الكلمات المفتاحية :- تربة ملوثة، الاستخلاص المتعاقب، الرصاص، النيكل، الكادميوم

1. INTRODUCTION

Soil is one component of environmental system; there are a lot of sources to their contamination with heavy elements, including factory chimneys, car exhausts, sewage waste, garbage, pesticides and chemicals [23]. There are elements in general, including heavy elements in several forms in soil some of them are soluble, and some of them are not and this depends on the nature of the interaction between heavy elements and mineral or organic soil components. These reactions are adsorption, reverse adsorption, sedimentation, solubility, ion exchange, substitution in the crystalline structure of minerals and, finally, the vital role. These reactions have a role in facilitation the movement of Heavy elements in the soil [2]. The use of sequential extraction or what is known as differentially provides us with better information about the mechanism of binding heavy elements with different soil components, Giving a clear perception of the images of heavy elements, (Soluble in water, mutual, associated with carbonates, associated with iron oxides and hydroxides, associated with organic matter, associated with clay)Identifying the type and ratios of heavy metals in the soil helps to judge the gravity of these elements in the soil in terms of toxicity and movement, Among many methods of sequential extraction or differential [27], is the best and most widely used method. Therefore, the aim of the research is to estimate the images of heavy elements (lead, nickel and cadmium) with each component from the soil components for the purpose of knowing the mechanism of real environmental impacts.

1. MATERIALS AND METHODS

The study area was selected within the western part of the Musayyib project in Babylon province in central Iraq between latitudes 32°18'33.45"N to 32°43'05.01” north and longitude 44°09'53.64"E to 44°18'03.01"E east. The field work included the selection of five soil locations at date of 1/20/2016, the first location (S1) which is located 1 km north of the Euphrates chemical plant (comparator). The second location (S2) which is at Al-Frat Chemical Factory (for comparison). The third location (S3) which is the middle distance between the Euphrates chemical Factory and Al Sadda Cement Factory and the fourth location (S4) at Al Sadda Cement Factory, and the fifth location (S5) is located 1 km south of Al Sadda Cement Factory. Soil samples were taken from the earlier locations at two depths of 0-30 cm and 60-30 cm. Soil preparation was done by drying, grinding, mixing and sieving through a 2 mm sieve. The soil texture was Silty Loam (sand between 310-90 and silt between 738-539 and clay between 172 -122 g.kg^{-1}), and the following chemical analyzes were performed as shown in Table (1):

- The degree of pH and electrical conductivity (EC) with the extract (1: 1) described in [24].
- Total carbonate minerals were estimated by the weight method described in [15].
- Organic matter is estimated by the wet oxidation contained in [17].

Table 1: Chemical soil traits

Locations	Depth (cm)	pH	Ec dS.m^{-1}	$CaCO_3$ g.kg^{-1}	O.M g.kg^{-1}	CEC cmol charge.kg^{-1}
S1	**0-30**	6.93	4.66	245.3	2.7	18.23
	30-60	7.11	1.30	262.1	1.9	17.80
S2	**0-30**	7.04	10.18	332.7	3.1	23.82
	30-60	7.03	12.80	301.8	2.0	20.18
S3	**0-30**	7.15	3.75	236.0	1.7	21.24
	30-60	7.21	3.87	233.1	0.8	22.05
S4	**0-30**	7.18	2.83	205.0	1.8	23.52
	30-60	7.20	2.01	211.9	1.0	19.36
S5	**0-30**	6.96	7.47	261.4	4.1	25.13
	30-60	7.10	7.64	259.2	1.9	21.58

- The exchange capacity of positive ions was estimated using sodium acetate and ammonium acetate which described in [17].

-**The heavy elements (lead, nickel, cadmium) associated with each soil component were estimated:** using the successive extraction method [27], Taken 1 g of dry soil (<2 mm) in the centrifuge tube (50 mL), the next stages were conducted as follows:

1. Extraction of exchange heavy elements: They extracted by adding 8 mL of 1 molar sodium acetate solution with degree of reaction is (pH = 8.2), then the mixture was stirred for one hour at 25 ± ºC.

2. Extract the heavy elements associated with carbonates: by adding (8 ml) of sodium acetate solution with pH (5) to the remaining part of stage (1) and stirring the mixture for 5 continuous hours.

3. Extract the heavy elements associated with iron oxides and hydroxides: by adding 20 ml of solution (0.04 molar) $NH_2OH.HCl$ with 25% (v / v) of HOAc acid to the remaining part of stage (2) and then placing the samples in a water bath temperature 96 ± 3

0C for 6 hours with stirring from time to time. This phase extracts heavy precipitated elements such as hydroxides and / or concentrates on non-crystallized oxides or hydroxides.

4. Extraction of heavy elements associated with organic substance:

This stage is divided into three steps:

a. Add 3 ml of HNO_3 solution and 5 mL of 30% H_2O_2 (Modifies the solution to an interaction number pH=2) to the remaining part of phase 3, and the samples shall be placed in a water bath of 85 ° C ± 2 ° C for 2 hours with intermittent stirring.
b. Add 3 ml of 30% H_2O_2 with reaction number (pH = 2) and then heat the samples in a water bath of 85 ± 2 ° C for 3 hours with intermittent stirring.
c. Add 5 ml of solution (3.2 molar) NH_4OAc with 20% (v / v) of HNO_3, then complete the volume to 20 mL and mix the mixture for 30 min at 25 ° C. At this stage, the heavy elements associated with organic substance are extracted by adsorption, complexity or chelates.

5. Extract the heavy elements associated with the clay:

by digesting the remaining part of stage (4) according to method [28].

In all stages, the leachate is separated using a centrifuge of 6000 cycles per minute for 20 minutes. The remaining parts are washed with 8 mL distilled water followed by a strong manual shaking. Then separated by using centrifuge to be ready for the next extraction. The collected solutions were measured by the Atomic Absorption Spectrophotometer (Shimadzu / AA-7000) in the Graduate Laboratory of the college of Science - Babylon University / Department of Life Sciences.

2. RESULTS AND DISCUSSION

- Sequential extraction of heavy elements of the soil of the study:

1. The Exchangeable

Table (2) shows the values of the heavy elements (lead, nickel and cadmium) in the Exchangeable image. The highest value of the Exchangeable lead at location S3 was 0.480 mg.kg^{-1} for the depth of 0-30 cm and 30-60 cm respectively. Other locations between 0.352 - 0.192 and 0.256-0.338 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively. The highest value of the Exchangeable nickel at location S3 and S5 was 1.956 and 1.929 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while the values of the nickel exchange in other locations ranged between 1.530 - 0.853 and between 1.154 - 1.530 mg.kg^{-1} for the depths of 30 - 0 cm and 60 - 30 cm Respectively, and the highest value for mutual cadmium at location S5 was 0.691 and 0.638 mg.kg^{-1} for the depth of 0-30 cm and 60-30 cm respectively, while the Exchangeable cadmium values ranged from 0.47 to 0.452 and 0.372-0.479 mg Kg^{-1} depth of 0 - 0 cm and 60 - 30 cm respectively. The results of Table (2) show that the values of heavy elements are low and even deep in the soil and these values are contrary for the CEC positive exchange values that are relatively high as shown in table (1). This is due to the fact that the value of the exchange capacity of positive ions cannot give a clear prediction of the adsorption of heavy elements in neutral soils, or that the ion exchange process Are not always dominant or influential in the adsorption process due to other processes such as precipitation, complexity and specific adsorption [5, 7, 25].

2. Associated with carbonate minerals

Table (3) shows the values of heavy elements, lead, nickel and cadmium associated with carbonate minerals. The highest value of carbon-associated lead in S4 and S1 was 0.970 and 1.115 mg.kg^{-1} for the depth of 0-30 cm and 30-60 cm respectively, While the lead values associated with carbonate minerals in the other locations ranged between 0.727 - 0.582 and 0.388 - 0.970 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively. The highest value of nickel associated with carbonate minerals at location S4 and S3 was 1.680 and 1.806 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while the nickel values associated with carbonate minerals in the other locations ranged between 1.505 - 1.078 and 0.953 - 1.605 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, and the highest value of cadmium associated with carbonate minerals at location S2 and S4 0.638 and 1.010 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while the values of cadmium associated with carbonate minerals in the other locations ranged between 0.691 - 0.479 and 0.213 - 0.771 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively.

Table 2: Concentration of lead, nickel and cadmium Exchangeable (mg.kg^{-1})

Locations	Depth (cm)	lead	nickel	cadmium
S1	**0-30**	0.256	1.078	0.452
	30-60	0.352	1.404	0.372
S2	**0-30**	0.256	1.530	0.452
	30-60	0.256	1.530	0.452
S3	**0-30**	0.480	0.853	0.452
	30-60	0.480	1.530	0.452
S4	**0-30**	0.192	1.956	0.479
	30-60	0.384	1.154	0.479
S5	**0-30**	0.352	1.330	0.6911
	30-60	0.384	1.930	0.638

Table 3: Concentration of lead, nickel and cadmium associated with carbonate minerals (mg kg$^{-1)}$

Locations	Depth (cm)	lead	nickel	cadmium
S1	**0-30**	0.582	1.154	0.532
	30-60	1.115	0.953	0.292
S2	**0-30**	0.727	1.505	0.638
	30-60	0.388	1.028	0.372
S3	**0-30**	0.582	1.380	0.691
	30-60	0.970	1.805	0.213
S4	**0-30**	0.970	1.680	0.611
	30-60	0.582	1.530	1.010
S5	**0-30**	0.679	1.078	0.479
	30-60	0.679	1.605	0.771

All the soil of the study is calcareous as shown in Table (1). So its carbon content is between 211.9 - 332.7 g.kg^{-1}. The most important characteristic of calcareous soils is the predominance of ions (OH^-, HCO_3^-, Ca^{2+}) in its soils solution that controls the overall chemical reactions taking place:

$$CaCO_3 + H_2O \longrightarrow Ca^{2+} + HCO_3^- + OH^-$$

The [5] assumed That Cd^{2+} cadmium ions may be associated to the bicarbonate ions available In a solution of the Diyala River contaminated with cadmium, forming a complex component of cadmium bicarbonate $CdHCO_3$, which has a very high correlation coefficient [16], Thus, this hypothesis can involve Pb^{2+} and Ni^{2+} ions bearing the same equivalence and charge, which may be complexes of Pb $(HCO_3)_2$ and Ni-Ni-Bicarbonate $(HCO_3)_2$, or these ions can be linked to the surfaces of carbonate minerals by chemical adsorption, the [21] showed that there is an affinity between the ions of heavy metals and carbonate metals depends on the ionic radius, In other words, any ion with an ionic radius approximates the diameter of the

$$X + CaCO_3 \xrightarrow{\qquad} X\,CO_{3\,(ads)} + Ca^{2+}$$

The comparison of semiconductors of lead ions Pb^{2+}=1.19 A°, nickel ions (Ni^{2+}= 0.70 A°) and cadmium ions (Cd^{2+}= 0.97A°) [30] We find that the cadmium ion has a high affinity to the replacement of calcium in carbon minerals to the convergence of ionic radius, This is evidenced by the results, as the concentrations of cadmium associated with carbonate minerals is less than the concentration of lead and nickel associated with carbonate minerals, demonstrating the validity of hypothesis [5], in general, the presence of calcium carbonate minerals in the soil leads to deposition (retention) of heavy element ions in the soil [18].

3. Associated with oxides and iron hydroxides

Table 4 shows the values of heavy elements lead, nickel and cadmium associated with oxides and iron hydroxides. The highest lead calcium ion (0.99 A°). The ion will replace the calcium ion in the carbonate minerals as follows:

value associated with oxides and iron hydroxides at location S3 was 0.873 and 0.824 mg.kg^{-1} for the depth of 0- 30 cm and 30-60 cm respectively, while the lead values associated with iron oxides and hydroxides ranged between 0.727-0.242 and 0.388-0.69 mg.kg^{-1} for the 0-30 cm and 60-30 cm respectively. The highest nickel value associated with oxides and iron hydroxides was at S1 and S5 2.383 and 2.257 mg.kg^{-1} for depth In contrast, while the values of nickel associated with iron oxides and hydroxides ranged from 2.232 - 1.605 to 1.304 - 2.232 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively. The highest value of cadmium associated with oxides and iron hydroxides at locations S5 and S3 was 1.063 and 1.170 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while the values of cadmium associated with iron oxides and hydroxides ranged between 0.984 - 0.691 and 0.611 - 1.143 mg.kg^{-1} for the depth of 0-30 cm and 30 - 60 cm respectively.

Table 4: Concentration of lead, nickel and cadmium associated with oxides and iron hydroxides (mg kg^{-1})

Locations	Depth (cm)	lead	nickel	cadmium
S1	**0-30**	0.242	1.605	0.930
	30-60	0.436	2.383	0.771
S2	**0-30**	0.727	2.232	0.691
	30-60	0.582	1.304	0.718
S3	**0-30**	0.873	2.107	0.718
	30-60	0.824	2.232	1.170
S4	**0-30**	0.582	1.981	0.984
	30-60	0.388	1.756	1.143
S5	**0-30**	0.388	1.906	1.063
	30-60	0.679	2.257	0.611

The amount of heavy elements associated with oxides and iron hydroxides was higher than the amount of heavy elements exchanged with carbonate minerals, This is due to the fact that oxides and iron hydroxides, despite the small amount in the soil, especially Iraqi soils because of the formative nature of the mother material of the Iraqi soil, which does not help the development of these soils due to the large and contain large quantities of salts, especially carbonates, However, these oxides, especially those that are Amorphous, have a high ability to correlate with heavy elements, despite their low presence. This is due to their higher surface area compared with clay. The iron oxides, especially the Amorphous, The clay has attributed this to an increase in its surface quality, this is confirmed by [27] as described oxides and iron hydroxides, especially the Amorphous ones as good clips Excellent Scavengers of heavy elements, Thus, this attribute reflects the environmental importance of these oxides, as they are important in their adsorption of the largest quantity of these heavy elements, especially in soil with a pH reaction rate higher than 7 [5, 12].

4. Associated with organic substance

Table (5) shows the values of the heavy metals lead, nickel and cadmium associated with organic matter. The highest lead value of organic matter at location S1 and S2 was 0.582 and 0.388 mg.kg^{-1} for the depth of 0-30 cm and 30-60 cm respectively, While the lead values associated with organic substance at other locations ranged between 0.533-0.242 and 0.291-0.338 mg.kg^{-1} for the 0-30 cm and 30-60 cm respectively. The highest value of organic substance-related nickel at S5 was 4.966 and 3.561 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while nickel values associated with organic substance ranged from other locations between 4.891 - 1.404 and 1.906 - 3.837 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively. The highest value of cadmium associated with organic substance at location S1 was 1.170 and 1.303 mg.kg^{-1} for the depth of 0-30 cm and 30 - 60 cm respectively, while the values of cadmium associated with organic substance in other locations ranged between 1.143- 0.851 and 0.930 - 1.090 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively.

Table 5: Concentration of lead, nickel and cadmium associated with organic substance (mg kg^{-1})

Locations	Depth (cm)	lead	nickel	cadmium
S1	**0-30**	0.582	1.404	1.170
	30-60	0.291	1.906	1.303
S2	**0-30**	0.242	2.458	0.851
	30-60	0.388	3.837	1.063
S3	**0-30**	0.533	4.891	0.984
	30-60	0.291	3.210	1.090
S4	**0-30**	0.533	2.483	0.904
	30-60	0.388	2.232	0.930
S5	**0-30**	0.291	4.966	1.143
	30-60	0.291	3.561	1.063

The content of Iraqi soil, including the soil of the study as shown in Table (1) of organic substance is low compared to other soil components, But this did not negate its role in the capture of ions of heavy elements, but that this substance, despite the lack of content showed a clear superiority in the retention of heavy elements [5] This is shown by the results as this high capacity of organic substance may be due to the familiarity and high preference for the organic substance of positive ions Special metallic minerals including (Cd^{2+}, Ni^{2+}, Pb^{2+}) [7, 10]. This is due to the fact that organic matter has a capacity of exchange of high ions, which is estimated to be about 300 cmol charge.kg^{-1} of organic substance [6]. The difference between the results and the soil depth can be attributed to the effect of the conditions surrounding the organic matter. The [8] showed that the humidity, the degree of reaction, the C / N ratio of the decaying substance, the quantity and quality of the clay are factors affecting the degradation of organic substance, As a result of an interaction between organic colloids and mineral colloids in the soil [6, 29]. This is explained by [5] on the first two assumptions that the predominance of montmorillonite in the soil can cause the reduction of the bio-decomposition of organic substance [8] which is negatively reflected in the provision of new charged surfaces, The second is that the formation of links or interactions between organic and mineral colloids (clay and oxides) can cause the closure of the available locations on the surface of the colloids, resulting in variation in the exchange capacitance values of the positive ions of those colloids, the [26] showed the environmental importance of organic substance in the holding and Reservation of heavy elements, which depends on the nature and composition of organic substance and the surrounding mineral and environmental conditions.

5. Associated with clay (Residual)

Table (6) shows the values of heavy elements (lead, nickel and cadmium) associated with clay. The highest value of clay-related lead at the locations of S5 and S4 was 0.582 and 0.436 mg.kg^{-1} for the depth of 0-30 cm and 30-60 cm respectively, while The lead values associated with the clay at the other sites ranged between 0.533-0.45 and 0.291-0.436 mg.kg^{-1} for the 0-30 cm and 30-60 cm respectively. The highest value of the clay-associated nickel at S2 and S4 was 6.546 and 4.715 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while the values ranged for nickel is associated with the clay at other sites between 5.292 - 2.031 and 1.580 - 4.163 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively. The highest value of cadmium associated with clay at site S3 was 1.409 and 1.303 mg.kg^{-1} for the depth of 0 - 30 cm and 30 - 60 cm respectively, while the values of cadmium associated with clay in other locations ranged between 1.249 - 1.223 and between 1.063 - 1.249 mg.kg^{-1} for the depths of 0 - 30 cm and 30 - 60 cm respectively.

Table 6: Concentration of lead, nickel and cadmium associated with clay (Residual) (mg kg^{-1})

Locations	Depth (cm)	lead	nickel	cadmium
S1	**0-30**	0.145	2.031	1.223
	30-60	0.436	4.163	1.143
S2	**0-30**	0.242	6.546	1.223
	30-60	0.388	1.580	1.063
S3	**0-30**	0.533	4.063	1.409
	30-60	0.436	3.988	1.303
S4	**0-30**	0.242	3.837	1.250
	30-60	0.436	4.715	1.250
S5	**0-30**	0.582	5.292	1.250
	30-60	0.291	3.511	1.090

The basis of the effectiveness of the clay is that it is being the only colloidal part that has adsorption trait and is of great importance in determining the physical and chemical properties of the soil [4, 6, 11]. The soil content from the clay is between 122 -183 g.kg^{-1} this amount is higher than the soil content of carbonate minerals, organic matter and even oxides and iron hydroxides, which, according to the results, resulted in the retention of this high quantity of heavy elements compared to the amount of heavy elements associated with carbon minerals Organic matter, oxides and iron hydroxides This is evident in nickel and cadmium elements, This is due to the exchange capacity of high-cation ions, especially with the predominance of high-capacity montormonlite metals, But these quantities of heavy elements exchanged on the minutes of clay is not high because of factors that also work to reserve quantities of these heavy elements such as organic matter and oxides and iron hydroxides and carbonate minerals. The nature of calcareous and saline soils have high calcium content and therefore there is competition occurs between calcium ions And the ions of heavy elements, especially ionic semiconductors similar to the radius of the calcium ion and therefore the sovereignty will be calcium compared to heavy elements and therefore the difficulty of replacing heavy elements replace calcium on the surface of soils, In other words, the dominance of the ion's influence in the case of competition depends on the concentration of the ion and the ionic radius [5, 21, 22]. Another explanation for the difference in the retention of clay for heavy elements is that there is a difference in the body in which carbonate minerals are present in these soils as they work to cover minutes of clay [5], the [9] showed that most of the minerals of carbonates in the Iraqi soil was in a single entity or a bond, A few of them were in the form of Covers around soft soil minutes (here mean mud minutes) and this is confirmed by [1] when studying the soil in central Iraq, Which is reflected on the efficiency of adsorption of clay minutes to those elements [5, 6, 13, 29, 31]. In general, the movement of heavy elements was regular and irregular (random) during the depths of the soil as it is decreasing or increasing within the soil and this may be due to the content of the component in which the heavy elements are linked, It may depend on the service and management of the soil from tillage, settling, irrigation and agricultural cycles, which has impacted the transport and redistribution of the soil components during the deep soil, which has been reflected in concentrations of heavy elements in the deep soil [5, 19, 29].

3. CONCLUSIONS

The overall concentration of the heavy elements in the soil does not give a clear picture of the toxicity or soil contamination by these elements so it is useful to estimate the images of these elements with each of the soil components to know the mechanism of the real environmental effects so the use of sequential extraction or what is known as differentially provides us with better information about Linking heavy elements with different soil components This helps to judge the gravity of those elements in the soil in terms of toxicity and movement.

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