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SEQUENTIAL EXTRACTION OF ZINC AND NICKEL ELEMENTS IN CONTAMINATED SOILS

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Abstract

In this study, a different textures of soil samples were taken from six sites nearby to the industrial facilities in Baghdad city, to study soil contamination with zinc and nickel elements and their forms in the soil using the sequential extraction method. The results showed that the soil components were different in the ability to reservation heavy metals depending on the amount of heavy metals, it's proportion in the soil, and the proportion and type of soil component. Based on the concentration of heavy metals, soil components can be arranged in the reservation of the two elements as follows: Carbonate minerals >Residues > Organic matter > Iron and Manganese oxides, while the Nickel was exceeding the Zinc by increasing its concentrations in different soil components.

Key words : Zinc, Nickel, Soils.

Introduction

With the diffusion of technology and the evolution of science, There has been a huge quantum leap for human by relying on the data of this technology in its various daily activities, these tools such as cars, airplanes, refineries, modern factories, electrical power stations, brick factories, etc. have a harmful residue to the environment and humans such as toxic and harmful gases, hydrocarbons, toxic heavy elements, radiation and others (Gharaybeh, 2010). These residues have dangerous effects, but heavy metals are considered as the most dangerous one, which is the silent killer, which spreads in three ways to the environment: Firstly, by air, where the chimneys of factories, refineries, brick factories and electrical power stations release many oxides element into the air that are contaminated and transmitted to the humans, animals, soil and plants (Al-Rubaie, 2014). Secondly, by water that's used in these industrial facilities for cooling, or finally, through the soil, these metallic elements are corroded by humidity and melts to water and rain, and it descend into soil layers, causing a contamination of groundwater sources and plants with these elements. These elements had many dangerous effects, including food, metal poisoning and various diseases, where founds in the soil in several forms, including the dissolved and the exchangeable, depending on the nature of the interaction between these elements and the components of the mineral or organic soil. These reactions include adsorption, release, deposition, ion exchangeable, and substitution in the crystal structure of minerals, and these reactions have an important role in the heavy metals availability and their movement in soil (Al- Farage and Al- Wabil 2009). The total concentration of heavy metals in the soil does not give a clear description of their toxicity, therefore, an evaluation of these elements that connected to each of the different soil components was carried out to understand the mechanism of their environmental impacts (Tessier *et al.*, 1979). Sequential extraction provides a good and useful information about the heavy metals that connected with different soil components and gave a clear description of these element forms, and its toxicity rang and mobility such as (dissolved in water, exchangeable, connected to carbonate minerals, connected with iron and manganese oxides, connected with organic matter, and connected with clay). Mclaughlin (2000) showed that the most of the heavy elements adsorbed on the surface of the soil particles mutually and then, over time, they turn into fixed form. (Abbas, 2018),

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explained the sequential extraction of the nickel element for a contaminated soil affected by the Al-Furaat plant for chemical production and Al-Sadaa cement plant activity, as follows: Carbonate minerals > Clay > Organic material > Iron oxides and hydroxides. The aim of the study was to estimate the Zinc and Nickel elements forms that connected with different soil components in contaminated soil with the activity of industrial plants.

Materials and Methods

Six different sites (agricultural or civilian) within the borders of Baghdad city were selected for a soil affected by the activity of some of the industrial plants such as, the brick factories in Al-Nahrawan District (ND), the battery plant in the Waziriya District (BP), Al- Dora Oil Refinery (DOR), Al- Dora first electrical power station (DFEPS), Al- Dora second electrical power station (DSEPS), Diyala Bridge District (DB) affected by the contaminated waters of the Diyala river. The soil was taken from the surface layer by 0-30 cm, then was dried, crushed, and sifted by a 2 mm sieve to conduct some of the physical and chemical analyzes as shown in Table 1 according to Bashour and Sayegh (2007) as follows: The electrical conductivity and soil interaction were estimated using EC-meter and pH-meter devices, while the cation exchange capacity of ions (CEC) using Ammonium acetate 1N at pH = 7. Moreover, the total carbonate minerals estimated using Hydrochloric acid (3N) by the calcimeter device according to(Hesse, 1971) method and the organic matter in the wet digestion method (wet digestion) according to the Walkly and Black method mentioned by (page *et al.*, 1985), in addition to the size distribution of soil particles using hydrometer device, as mentioned in (Black *et al.,* 1965).

The available concentration of the Zinc and Nickel elements was estimated by extracting them from the soil by the Diethylene triamine penta acetic acid (DTPA) according to (Lindsay and Norvell 1978) and then measured by the Atomic Absorption Spectrometer. The total content of the two elements mentioned previously in the soil was estimated after sample digestion using ($HCLO_{4-}$ HNO_3) acid mixture, by taking one gram of the sample which was air dried and sifted by a 2 mm diameter sieve and placed in a 250 ml pyrex glass bottle, then a 5 ml of concentrated nitric acid HNO_3 was added and left for 24 hours. The samples were placed on a hot plate at 80 ° C for 1 hour, then cooled aerially and a 5 ml of $HCLO_4$ was added and placed on a hot plate at 180 ° C for 2-3 hours till the color changed from dark brown to clear colorless solution. Finally, it was filtered by N0.42 Whatman filter paper and the size completed up by a 50 ml distilled water to achieve the measurement Atomic Absorption Spectrometer device.

The sequential extraction for Zinc and Nickel, which they are exchangeable and connected_to soil separates was carried out in accordance to Kashem *et al.,* (2007) methods by taking a one gram of dried soils sifted by a 2 mm sieve then put it into a 50-ml polyethylene tube, including the following four stages:-

1. Zinc and Nickel extraction that exchangeable and connected to carbonates: -

Extracted by using a 40 ml of 0.11 M from CH_3COOH solution, then, it mixed for 16 h.

2. Zinc and Nickel extraction that connected with iron and manganese oxides:

by adding 40 ml of $NH_2OH.HCL$ solution with pH = 2 and it mixed for 16 hours.

3. Zinc and nickel extraction that connected with the organic matter

By adding a 10 ml of the 8.8M solution from H_2O_2 to the residual element of stage 2, then after one hour it heats up to 90 ° C for 1 hour and then, a10 mL of 8.8M solution of H_2O_2 was added and heats up again to 90 ° C for 1 hour. The mixture was then cooled and 50 ml of 1M ammonium acetate added and mixed for 16 hours at room temperature. This stage, involves Zinc and Nickel extraction which they were deposited as hydroxides, or adsorbed on oxides or non-crystallized hydroxides.

4. Residual Zinc and Nickel extraction : -

Obtains by subtraction of the three extracted elements from the total concentration.

Results and Discussion

Zinc connected with soil separates

Exchangeable, zinc connected to carbonate minerals

The results of table 2 shows a variation in results values ranging from 19.68 to 47.60 mg Zn/ Kg soil with a general rate of 41.48% of total zinc, the highest value was recorded in the DOR by 47.60 mg Zn/ kg soil while the lowest values in the soil of the DSEPS amounted to 19.60 mg Zn/kg soil. This can be attributed to the soil of the DOR contains the highest percentage of carbonate minerals by 33.17%, while the lowest values in the DSEPS because it contains the lowest amount of carbonate minerals by 27.23%. These results were agreed with Kabata and Pendias (2001) findings, which that the presence of carbonate minerals in the soil leads to deposition (reservation) of heavy metals ions. In addition to the large contamination caused by the DOR in the

Table 1: Some physical and chemical properties of the study soil.

Seq.	Sample site	pH	ECdS.m^{-1}	Carbonate minerals%	Organic matter mg/kg	Soil texture	Clay ratio%	Silt ratio %	TotalZn	Available Zn	Total NI	Available NI
1	ND*	7.36	1.40	31.94	0.73	Silt loam	12.00	70.80	82.66	2.03	115.18	0.84
2	BP*	7.21	3.20	29.81	0.61	Sandy loam	12.40	14.00	69.07	4.16	108.76	10.22
3	DOR*	7.30	2.33	33.17	0.74	Silt loam	18.00	56.80	10.17	5.98	123.66	2.83
4	DFEPS*	7.48	4.90	30.11	0.61	Silt loam	22.00	54.80	74.02	5.98	103.88	2.88
5	DSEPS*	7.20	3.60	27.23	0.65	Sandy loam	18.20	26.00	64.24	10.04	95.99	10.35
6	DB*	7.46	4.40	31.10	0.71	Sandy clay loam	20.00	48.80	83.36	4.15	106.27	0.83

Note:-
ND refers to in Al-Nahrawan District
the batteries plant in Waziriya District (BP)
Al- Dora Oil Refinery (DOR)
Al- Dora first electrical power station (DFEPS)
Al- Dora second electrical power station (DSEPS)
Diyala Bridge District(DB)

Table 2: Zinc concentrations (mg / kg) as a result of sequential extraction.

Seq.	Sample site	Connected to carbonate	Connected to iron and manganese oxides	Connected to organic matter	Connected to residual clay	Total
1	ND	41.3	2.93	15.49	20.91	82.66
2	BP	25.31	4.73	13.15	21.72	69.07
3	DOR	47.60	3.26	20.94	24.39	102.17
4	DFEPS	27.44	2.84	11.37	26.39	74.02
5	DSEPS	19.68	3.77	12.43	18.32	64.24
6	DB	36.00	4.90	16.18	22.13	83.36

nearby soil due to gaseous emissions and the heavy elements vapors from the refinery (Galibi, 2016).

Zinc connected to Iron and Manganese Oxides

Table 2 shows a variation in results values, ranging from 2.84 to 4.90 mg Zn/ kg soil with a general rate of 4.70% of total zinc. The highest values were recorded in the soil of the DB were 4.90 mg Zn/ kg soil, while the lowest values in the soil of the DFEPS amounted to 2.84 mg Zn/ kg soil. The increment in the DB soil may be due to that the contamination of the area increased by the element as a result of irrigation with polluted water of the Diyala river resulted from the releasing of waste water coming from Al-Rustumiya station. These results were agreed with Juma and Anbari (2010) findings, which they indicated to the contamination of the Diyala River with some heavy metals, including zinc, as a result of releasing waste water from the Rustamiyah station. The results also showed that the amount of zinc connected to iron and manganese oxides is little compared with the amount connected to carbonate minerals, this may be due to what (Mashhadani, 1994) explained, that the amount of iron oxides in Iraqi soils were little because of the material composition nature forming of the Iraqi soil, which doesn't help to develop this type of soil because their modernity and high content of salts, especially carbonates. Therefore, the adsorbed of heavy metals with oxides are few (Abbas, 2018).

Zinc connected to organic matter

The highest values were recorded in the soil of the DOR amounted to 20.94 mg Zn/ kg soil and the lowest values in the soil of the DFEPS were amounted to 11.37 mg Zn/ kg soil, with a general rate of 18.82% from total zinc as shown in Table 2. The reason for the increase in zinc related to the DOR soil may be due to an increase in the percentage of its organic matter by (0.74%) compared to other soils, in addition to gaseous emissions and the heavy metals vapors from the refinery that increase the concentrations of these elements in the soil. Also an increase in the amount of zinc that connected to organic matter was observed compared to that connected to oxides, which may be due to the familiarity and preference of the organic matter for connecting to metal ions, especially, bilateral shipment (Adriano *et al.,* 2002 and Hamzah, 2005) to increase the exchange capacity of cation ions in organic matter compared to oxides. These results were agreed with the results of Al- Awsy(2014), which showed an increase in the amount of zinc connected to organic matter by increasing its existence in the soil.

Residual zinc in the crystalline structure of clay minerals

The Zinc concentrations that connected or exist in the crystalline mineral structure represent the non-finished form, which is a relatively stable and inactive phase (Gismera *et al.,* 2004). The Zinc residual concentrations ranged from 18.32 to 26.39 mg Zn/ kg soil at a general rate of 28.15% from the total Zinc concentration, while the highest values in the soil of the DFEPS were 26.39 mg/ Kg and the lowest values in the soil of the DSEPS amounted to 18.32 mg/ Kg as shown in Table 2. This was due to the high percentage of clay which separates in the DFEPS soil amounted to 22.00%, while the percentage of the DSEPS soil was 18.20%. The clay is the important mineral colloid part, which characterized by adsorption because it has a high exchange capacity for cation ions, especially with the predominance of clay minerals 1: 2, (Awad, 1986). In comparison, of the adsorption amount on clay particles with that connected to carbonate minerals, an increasing was found in the amount of that connected to carbonate minerals because of the nature of the Iraqi calcareous soil and its high content of carbonate minerals (FAO, 1973). Based on the results of this study, the connected zinc form with separates soil can be arranged as follows: Minerals Carbonates > Residual > Organic matter > Iron and manganese oxides, respectively % 41.48 > 28.15% >18.82% >4.70%

Nickel connected to separates soil

Exchangeable nickel connected to carbonate minerals

The results in table 3 showed that there was a variation in nickel connected to carbonate minerals value , where the highest values was recorded in the DOR soil, which reached 51.90 mg Ni/ kg while the lowest values were in the DSEPS soil at 31.00 mg Ni/ kg, with a general rate of 37.86% of the total nickel concentration. The reason behind the increase in the refinery soil may be due to the amount of carbonate minerals in it, which reached 33.17% compared to the rest of the study soil as shown in table 1, in addition to the large pollution caused by the refinery in nearby soils (Al- Galibi, 2016). In general, the presence of carbonate minerals in the soil leads to deposition of heavy metals ions in the soil (Kabata, Pendias, 2001 and Abbas, 2018).

Nickel connected to iron and manganese oxides

There was a huge variation in the values depending on the location of the study soil as shown table 3, where the highest values were recorded at the nearby soil to the BP at 7.63 mg/ kg soil, while the lowest values in the ND soil amounted to 0.89 mg/ kg soil, with a general rate equal to 2.29% of the total nickel concentration. That increasing in the nickel concentration connected to iron and manganese oxides in the BP soil may return to the plant site which was located in an industrial area, where many factories and plants, such as smelting metals, coatings and other factories, which leads to an increased in gas emissions and vapors that contain some heavy elements such as nickel and their accumulation in nearby soils Wuana and Okieimen (2011). This was agreed with (Al-Halafi, 2010), which shows that there was an increase in heavy element concentrations in nearby soils to industrial areas. The environmental pollution of the soil depends on its distance from the pollution sources and the loss of portable pollutants with gases emitted from the chimneys of factories and plants containing heavy metals.A decrease in the connected amount of the oxides was observed compared with those connected to other separates soil due to the decrease in the amount of these oxides in Iraqi soils (Mashhadani, 1994). These results present good agreement with (Abbas, 2018) finding, which shows a decrease in the amount of nickel connected to oxides compared with those connected to other separates soil, this was due to the low presence of these oxides in Iraqi soil.

Nickel connected to organic matter

The results of table 3 indicate variation in the values of the nickel connected to organic matter, ranging from 21.35 to 29.65 mg/ kg with a general rate of 25.74%, forming a percentage of 23.62% from the total nickel. the highest values were in the DOR soil amounted to 29.65 mg/ kg and the lowest values in the DFEPS soil at 11.37 mg/kg, this may be due to that the huge pollution which caused by the refinery to the nearby soil. This was agreed with the results of Al-Anbari (2013), which pointed to the presence of large pollution in the nearby soils from the DOR with some heavy elements, including nickel by gases and vapors rising from the refinery and weighed with large amounts of heavy metals falling on the nearby soils, as well as, increasing in the proportion of organic matter in the soil of the refinery compared to the other soils as shown in Table 1.

Table 3: Nickel concentrations (mg / kg) as a result of sequential extraction.

Seq.	Sample site	Connected to carbonate	Connected to iron and manganese oxides	Connected to organic matter	Connected to residual clay	Total
1	ND	45.50	0.89	28.91	39.04	115.18
2	BP	33.90	7.63	27.65	29.46	108.76
3	DOR	51.90	1.24	29.65	38.04	123.66
4	DFEPS	41.30	1.23	21.35	37.12	103.88
5	DSEPS	31.00	2.98	22.70	28.96	95.99
6	DB	43.90	1.03	24.20	36.31	106.27

Residual nickel in the crystalline structure of clay minerals

This section represents the non-available quantity of the element because it represents a relatively stable and inactive phase (Galan *et al.,* 2003). The results in table 3 show that the concentrations ranged from 28.96 to 39.04 mg / kg at a general rate of 34.82 mg / kg, while it reached 31.95 % of the total nickel concentration. The highest values in the ND soil amounted to 39.04 mg/ kg and the lowest values in the DSEPS soil amounted to 28.96 mg/ kg. This may be due to the rising gas and vapors from the brick factories in Al- Nahrawan, and weighed with large amounts of heavy elements as a result of their use of heavy fossil energy in combustion processes. This was agreed with Al- Galibi (2016) findings, who pointed to the presence of large pollution in the nearby soils from the ND with nickel, as a result of emitted gases and vapors from these plants which are weighed with heavy elements such as nickel. Based on the results above, then connected to nickel form with separates soil can be arranged as follows: Minerals Carbonates > Residual > Organic matter > Iron and manganese oxides, 37.86% > 31.95%> 23.62% >2.29%, respectively. These results present a good agreement with (Abbas 2018) findings.

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