EFFECT OF MINERAL COMPOSITION ON SEQUENTIAL EXTRACT OF LEAD AND CADMIUM IN SOME IRAQI SOILS

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ABSTRACT

This study was aimed to find out the effect of different soil components of some Iraqi soils under different climatic conditions and different parent materials on the adsorption of lead and cadmium. Soil samples were collected from four governorates (Dohuk, Wasit, Salah al-Din, and Basra), with three sites in each governorate, and two depths (0-30 and 31-60) cm. A chemical analysis of the soil were carried out to determine the amount of organic matter, carbonate minerals, total and crystallized free iron oxides. Results showed that the values of and soluble and exchangeable lead binded with carbonate minerals, organic matter, oxides, and clay fraction in rates ranging between (0.27-1.04), (0.83-1.51), (18.81-41.58), (2.31-21.95), (3.93-23.75), and (5.65-5). 67.83)% respectively of the soil content and the values of the coefficient of determination R^2 (0.86, 0.16, 0.72, 0.79, 0.40, and 0.69), respectively. As for the cadmium element, the results showed that its values were (0.49-1.66), (1.13-2.47), (40.24-79.51), (0.24-7.98), (3.25-36.76) and (6.74-38.24)% for the soluble ,exchangeable and binded with carbonate minerals, organic matter, oxides, and clay fraction respectively.

Keywords: carbonate minerals, organic matter, oxides, clay minerals.

تأثير التركيب المعدني في الاستخلاص المتعاقب لعنصري الرصاص والكادميوم في بعض الترب العراقية

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المستخلص

هدفت هذه الدراسة لمعرفة تأثير مكونات الترب المختلفة لبعض الترب العراقية الواقعة تحت تأثير مختلف من الظروف المناخية ولمواد اصل مختلفة في ارتباط عنصر الرصاص والكادميوم. إذ تم جمع نماذج الترب من اربع محافظات (دهوك, واسط, صلاح الدين, البصرة) وبواقع ثلاث مناطق لكل محافظة ولعمقين (0−30 و 31−60) سم . تم اجراء التحليل الكيميائي للترب لمعرفة كمية مكوناتها من المادة العضوية, معادن الكاربونات, أكاسيد الحديد الحرة الكلية والمتبلورة. أظهرت النتائج أن قيم الرصاص الذائب والمتبادل والمرتبط بمعادن الكاربونات والمادة العضوية والاكاسيد والطين بنسب تراوحت بين (0.27−1.04) و(0.83−1.51) و(18.81−41.58) و(2.31−21.95) و(3.93−23.75) و(5.65−67.83)% من محتوى التربة من الرصاص الكلي. وبقيم معامل تحديدR^2 (0.86 و0.16 و 0.72 و 0.79 و0.40 و 0.69) بالتتابع . اما بالنسبة الى عنصر الكادميوم فقد أظهرت النتائج أن قيمها كانت (0.49−1.66) و(1.13−2.47) و(40.24−79.51) و(0.24−7.98) و(3.25−36.76) و(6.74−38.24) % لكل من الذائب والمتبادل والمرتبط بمعادن الكاربونات والمادة العضوية والاكاسيد ومعادن الطين على التوالي.

الكلمات المفتاحية: معادن الكاربونات , المادة العضوية, الاكاسيد ,معادن الطين

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INTRODUCTION

Soils vary clearly in their chemical, physical, and biological properties, depending on the variation in the type of parent materials that formed soils, topography, type and nature of exploitation, and the overall climatic conditions associated with the processes of their formation, and then their development over time. The mineral composition of the soil reflects the nature of its various basic components, represented by clay minerals and carbonate minerals, their content of organic matter and oxides, the proportions of their fraction, and the evolutionary path that they reached over time. Thus, minerals are created and formed in the soil by exposing the primary rocks constituting the earth's crust to several processes, which may naturally differ in the severity of their occurrences such as weathering and transformation (4,11,14,16). indicated that heavy elements such as lead, cadmium, etc... spread in the soil naturally as a result of the occurrence of pedogenic processes, erosion, and weathering in the parent rocks containing certain proportions of these elements during the formation and development of the soil. The other source for the presence of these elements in the soil is the dust of storms and volcanoes, in addition to the great role played by various industrial human activities through the combustion of fuel of all kinds and sewage water (14,19) .confirmed that the cadmium element is found naturally among the components of some soils, in relatively small quantities, and rarely reaches toxic levels in special cases, and that the direction of the behavior of these elements in the soil is affected by many factors, the most important of which is the soil reaction number, and its content of organic materials, the quantity and quality of clay minerals prevailing in them, their content of oxides, and their ionic exchange capacity. The presence of heavy elements in the soil is similar to the presence of the rest of other nutrients in the soil, and it takes different forms, it may be in the form of soluble in the soil solution or adsorbed on the constituent surfaces of the soil of various types, or with organic matter in a state of complexity, the proportions of the presence of these forms are affected by the total amount of them in the extent of its effectiveness and activity, and thus its relative movement in the soil, and then the extent of its availability for plants (1,5). The total concentrations of heavy elements in the soil do not give a clear picture of the amount of harmful effects they cause. To overcome this, it has become necessary to estimate the forms of heavy elements with each of the main soil components, and to identify their real effects on the environment and then on humans. As the two soluble and exchange forms are the fast-moving and processing forms, which are facilitated by the time when the forms of the elements correlated with clay minerals, carbonates, organic materials, and free oxides of iron are relatively less active, and this activity depends mainly on the quantity and nature of those components. Therefore, sequential extraction can be considered one of the good and promising methods for assessing the extent of soil contamination with heavy elements by giving a clear perception of the different forms of heavy elements prevailing in the soil and their correlation with the different soil components, and then reaching more modern and efficient methods in management to reduce pollution in contaminated soils or that are continuously exposed to pollution (8,17). Familiarity with the mechanisms by which the heavy element will be correlated to the soil body is the first correct step in tracing the fate of that element in the soil structure, and then the extent of its availability and movement in the soil sector as a whole. Therefore, it became necessary to identify the dynamics of the geochemical processes occurring in the soil as an open natural system, as it is the organizer of the process of movement and transmission of various elements, including heavy elements. As the mechanisms for holding the heavy elements in the soil body depend on the extent of the ability of the surfaces of mineral and organic colloids, carbonate minerals, and free iron oxides to hold and retain these elements through ionic forces, electrostatic or covalent bonds, and Van der Waals forces, which determine their movement and spread in the soil sector as a whole, depending on the properties solid surfaces and their concentration in the soil solution or through the interactions of those heavy elements with the active carboxylic and phenolic aggregates of organic substances and the formation of complexes (complexing reactions). The nature of interactions of heavy elements with surfaces charged only with negative or positive charges includes adsorption, precipitation, and complexation (7,26). This study was aimed to find out the effect of the different mineral and organic soil components on the behavior of lead and cadmium, this research was conducted.

MATERIALS AND METHODS

Soil samples were collected from several regions of Iraq, different in their formation and environmental conditions surrounding them from north to south, from four provinces (Dohuk, Salah al-Din, Wasit, and Basra) and from three sites in for each province at depths of (0-30 and 31-60)cm. the collecting samples were air dried,crashed, and passed through the sieve of 2mm openings then some chemical and physical analyses were done on it , as show in Table 1 as stata by (25). Mineral analysis of soils was also carried out using x-ray technique to determine the mineralogical composition of those soils. Soil samples were incubated in a laboratory after treatment with lead and cadmium at a concentration of 40 mg.kg^{-1} soil, using lead chloride and cadmium sulfate, and exposing them to successive periods of drying and wetting at depleting 75% of the available water at the Laboratory temperature (28-32) °C. After 120 days of incubation, sequential extraction of lead and cadmium was carried out. The soluble and exchangeable lead and cadmium binded with carbonate minerals, oxides, organic matter, and total were extracted, while the amount binded with clay minerals was calculated by subtracting the total amount from the binded with components previously referred to according to the (21,28). The statistical analysis of the data was conducted using the Statistical Analysis System 2022 and finding the regression coefficient for the characteristics dependent on the different factors of soil components and finding equations for simple and multiple predictions and the coefficient of determination (R^2) to find out what are the most influential components in each element, as **X**1 = clay percentage and **X**2 = total carbonate minerals, **X**3= active carbonate minerals, X4 = organic matter, **X5** = total iron oxides, and **X**6 = crystalline iron oxides.

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

Governorate	Region	Depth Cm	Sand g kg^{-1}	Silt g kg^{-1}	Clay g kg^{-1}	pH	ECe Ds.m^{-1}	Carbonate minerals g kg^{-1}	Active lime g kg^{-1}	Gypsum g kg^{-1}	Organic matter g kg^{-1}	Total iron oxid g kg^{-1}	Amorphou g kg^{-1}
	Amadiah	0-30	283.6	374.1	342.3	7.5	0.86	98.7	52.0	3.5	36.2	3.52	0.06
		31-60	313.6	335.2	351.2	7.8	0.97	189.9	84.3	2.6	22.9	3.31	0.04
Duhok	Aqrah	0-30	293.6	336.4	370.0	7.6	0.75	117.1	67.0	5.9	38.5	5.26	0.08
		31-60	263.6	339.4	397.0	7.7	0.97	141.7	72.4	3.8	25.2	5.23	0.08
	Smell	0-30	293.6	296.4	410.0	7.5	1.05	279.5	71.1	4.5	32.3	4.56	0.06
		31-60	112.0	230.0	658.0	7.7	1.99	359.9	121.2	0.7	6.9	4.31	0.05
	Essaouira	0-30	113.0	127.0	760.0	8.0	112.79	220.8	115.5	20.3	24.5	3.20	0.04
		31-60	155.3	135.7	709.0	7.7	43.90	298.9	105.2	12.7	14.8	0.31	0.03
Wasit	Kut	0-30	187.5	376.5	436.0	7.3	65.10	271.7	85.7	28.4	21.8	3.81	0.04
		31.-60	190.2	399.8	410.0	7.6	17.68	338.3	100.2	29.3	15.1	3.38	0.04
	Numania	0.-30	245.7	367.3	387.0	7.2	37.33	300.5	95.8	48.4	30.2	3.21	0.03
		31-60	250.8	348.2	401.0	7.5	18.69	358.6	100.7	27.4	11.8	0.36	0.03
	Shirqat	0-30	99.0	521.0	380.0	7.8	2.99	173.9	24.3	103.0	15.1	4.98	0.08
		31-60	103.0	500.0	397.0	7.9	4.15	190.4	87.5	128.9	16.1	4.73	0.07
Salahaddin	Al Faris	0-30	567.0	261.0	172.0	7.7	5.15	83.3	50.4	305.2	3.7	0.15	0.03
		31-60	591.0	213.0	196.0	7.7	4.78	48.2	25.5	319.0	0.7	0.13	0.03
	Al Dur	0-30	618.0	239.0	143.0	7.6	4.10	72.0	55.7	323.8	1.7	0.68	0.03
		31-60	625.0	235.0	140.0	7.8	3.98	61.9	37.5	354.5	1.5	0.20	0.03
	Zubair	0-30	580.4	239.0	180.6	7.6	16.20	73.2	37.2	251.4	13.1	0.13	0.04
		31-60	571.0	251.0	178.0	7.5	10.98	79.1	30.9	211.5	5.0	0.15	0.04
Basra	Al Qarna	0-30	676.4	149.0	174.6	7.6	17.34	77.3	35.2	218.2	8.4	0.06	0.02
		31-60	616.0	198.0	186.0	7.7	8.20	76.0	30.2	237.6	1.0	0.23	0.03
	Al Der	0.30	629.0	172.0	199.0	7.8	4.78	70.8	45.8	237.7	0.7	0.07	0.02
		31-30	680.0	129.0	191.0	7.7	4.70	75.0	30.7	166.0	15.11	0.09	0.02

Table 2. The dominance of clay minerals in the study soils

Governorate	Region	Depth cm	Arrangement of minerals according to the dominance
Duhok	Amadiah	0-30	Smectite > Mica > Chlorite > Kaolinite
		31-60	Smectite > Mica > Kaolinite > Chlorite
	Aqrah	0-30	Smectite > Mica > Chlorite > Kaolinite
		31-60	Smectite > Mica > Chlorite > Palygorskite> Kaolinite
	Smell	0-30	Smectite > Mica > Chlorite > Kaolinite
		31-60	Smectite > Mica > Chlorite > Kaolinite
Wasit	Essaouira	0-30	Smectite > Mica > Chlorite > Kaolinite
		31-60	Smectite > Mica > Chlorite > Kaolinite
	Kut	0-30	Smectite > Mica > Chlorite > Kaolinite
		31-60	Smectite > Mica > Chlorite > Kaolinite
	Numania	0.-30	Smectite = Mica > Chlorite > Kaolinite
		31-60	Smectite > Mica > Chlorite > Kaolinite
Salahaddin	Shirqat	0-30	Smectite > Mica > Chlorite > Palygorskite > Kaolinite
		31-60	Smectite > Chlorite > Mica > Kaolinite > Palygorskite
	Al Faris	0-30	Mica > Smectite > Palygorskite > Chlorite > Kaolinite
		31-60	Mica > Smectite > Palygorskite > Kaolinite > Chlorite
	Al Dur	0-30	Mica > Palygorskite > Smectite > Kaolinite > Chlorite
		31-60	Mica > Palygorskite > Smectite > Kaolinite > Chlorite
Basra	Zubair	0-30	Palygorskite > Mica > Smectite > Chlorite > Kaolinite
		31-60	Palygorskite > Mica > Chlorite > Smectite > Kaolinite
	Al Qarna	0-30	Mica > Smectite > Chlorite > Kaolinite
		31-60	Mica > Kaolinite > Chlorite > Smectite
	Al Der	0-30	Mica > Chlorite > Smectite > Kaolinite
		31-60	Mica > Smectite > Chlorite > Kaolinite

RESULTS AND DISCUSSION

Sequential Extraction of Lead

Tables **3** and **4** show the concentration values of different forms of lead in the study soils before and after adding lead at a concentration of 40 mg.kg^{-1} and exposing it to successive cycles of wetting and drying for 120 days. The results showed that the percentages of the presence of soluble lead ions in the soil solution after the addition ranged between (0.27-1.04)% of the total concentration, as there was a highly significant positive correlation (**) of the soluble lead ions with the soil content of the clay fraction relative to the rest of the other main soil components, with a coefficient of determination (R^2) = 0.86. It also found a highly significant positive relationship (**) for the soluble lead with organic soil materials, with a coefficient of determination (R^2) = 0.78 this is concerning the simple linear correlation. As for the multiple relationships, a significant positive correlation (*) was found with a coefficient of determination (R^2) = 0.28 for the soluble lead with the main soil components combined according to the following equation: - Since Y^= soluble lead

Y^=0.53-0.0002933X1+0.00021163X2+0.00021902X3-0.00510X4-0.01191X5-0.62090 X6

The percentages of the presence of exchangeable lead after addition ranged between (0.83-1.51)% of the total concentration, as a positive significant correlation (*) was found for the exchangeable lead ions with the soil content of clay relative to the rest of the other soil components with a coefficient of determination (R^2) = 0.16. This is concerning the simple linear correlation, but in the multiple correlations, a non-significant relationship (NS) was found for the exchangeable lead with the main soil components combined with a coefficient of determination (R^2) = 0.15, and this was found by Ahmed and Abdel-Razzaq (3) according to the following equation:- Y^= exchangeable lead

Y^=0.87-0.00019270X1-0.00017818X2+0.00085692X3-0.00237X4-0.00878X5-0.08688 X6

The percentages of the presence of lead ions correlated with carbonate minerals after addition ranged between (18.81-41.58)% of the total concentration, and they came in agreement with the soil content of total carbonate minerals, which ranged between 48.02-359.9 g.kg^{-1} soil and active lime between 24.3-121.2 g.kg^{-1} soil, which is the most active part of carbonate minerals, and these percentages are high compared to the total quantities of lead in the soil. As the adsorbed amount of heavy elements such as lead increases in the soil with an increase in its concentrations added to the soil, the soils vary in their ability to adsorb and release various elements, including heavy ones, as a result of their variation in chemical and physical properties, their content of carbonate minerals, the amount and type of colloids, the amount of organic matter they contain, the ionic strength, and pH. It was noted from the results that there was an increase in the percentages of lead ions correlated with carbonate minerals, as the soils are naturally calcareous and formed from calcareous parent materials, as a highly significant positive correlation (**) was found between lead ions correlated with carbonate minerals in the soil and its active lime content relative to the rest of the other soil components with a coefficient of determination (R^2) = 0.72 concerning the simple linear correlation. However, in the multiple correlations, a highly significant positive correlation (**) of lead ions correlated with carbonate minerals was found with the main soil components combined with a coefficient of determination (R^2) = 0.79 according to the following equation: - Since Y^= lead correlated to carbonates

Y^=13.52+0.00428X1+0.00417X2+0.10645X3-0.09377X4-0.80574X5+21.54429X6

These result are in agreement with finding of Al-Hassoon et al (7) Al-Rubaie & Al-Owaidy(12)and Al-Shammari (15) who have confirmed that carbonate minerals in soils have an active and effective role in the adsorption and retention of the majority of lead ions, and in general when soils contain high amounts of carbonate minerals, especially as an active lime, will lead to an increase in the adsorption and precipitation of heavy metals ions and their retention in the inactive form in the soil, which positively affects the reduction of pollution. The percentages of lead ions correlated to organic soil materials after addition ranged between (2.31-21.95)% of the total concentration of lead. These results agreed with the soil content of organic matter in quantity and quality, as it varied in the soils of the study according to the amount of organic matter contained in those soils, the soil content of organic matter ranged between 0.7-38.5 g.kg^{-1} which reflects the extent of the environmental importance of the organic matter in holding and retention lead ions and reducing their availability in the soil solution. This also depends in turn on the type and nature of the composition of organic materials and the overall mineral and environmental conditions. surrounding it Naser & Ibrahem (24) and Tsai et al (29) as lead naturally tends to form complexes with organic soil materials with different degrees of stability with the availability of appropriate conditions. Al-daini & Naser(6) and Al-Hilfi (10) referred to the active role played by the percentage of organic colloids present in the soil in determining the significant nature of the correlation between lead and organic materials, since the presence of organic materials in the soil with mineral colloids (clay and silt) will inevitably lead to the formation of complexes as a organic-Mineral complexes. Also, the incubation period, which lasted 120 days, and the exposure of the soil to successive cycles of wetting, drying, and temperature changes had an effective effect on increasing the oxidation and decomposition processes of the organic soil materials, and then on the correlation percentage of lead with those materials, and through the simple linear correlation coefficient, a highly significant positive relationship (**) was found with a coefficient of determination (R^2) = 0.40 for lead ions correlated with the organic matter with the soil content of organic matter.

Table 3. Shows the total concentrations of lead in mg.kg^{-1} and the percentages of the presence of the Pb forms in the soil before the addition

Governorate	Region	Total mg kg^{-1}	Soluble	Exchangeable	% binded with Carbonate minerals	% binded with organic mater OM	% binded with oxides OX	% Remainin in clay
Duhok	Amadiah	34.40	0.12	0.22	9.29	8.61	6.31	9.85
		31.92	0.11	0.22	10.34	4.93	5.94	10.38
	Acrah	41.89	0.15	0.24	8.22	13.97	9.85	9.46
		30.80	0.13	0.28	9.97	6.39	7.11	6.92
	Smell	35.61	0.13	0.23	11.00	5.99	6.84	11.42
		38.38	0.13	0.25	13.80	3.85	6.19	14.16
	Essaouira	37.88	0.29	0.38	13.63	4.75	1.99	15.84
		41.50	0.19	0.39	14.71	3.00	2.40	20.81
Wasit	Kut	42.37	0.30	0.49	11.26	3.98	5.70	20.64
		31.86	0.26	0.34	11.89	3.39	3.91	12.58
	Numania	36.58	0.37	0.49	12.37	5.68	2.12	15.55
		42.04	0.25	0.39	13.62	2.93	5.60	19.25
	Shirqat	39.36	0.20	0.40	5.09	3.25	6.98	23.44
		41.36	0.19	0.39	11.85	3.43	6.78	18.72
Salahaddin	Al Faris	31.72	0.27	0.52	6.51	2.76	2.27	19.39
		25.25	0.20	0.41	5.55	2.01	2.95	14.13
	Al Dur	18.69	0.17	0.32	3.99	1.22	1.33	11.66
		22.82	0.26	0.58	5.73	2.18	2.66	11.41
	Zubair	31.62	0.31	0.55	6.21	3.13	2.55	19.14
		22.20	0.19	0.40	6.11	2.11	2.74	10.65
Basra	Al Qarna	33.14	0.30	0.54	6.17	2.20	3.20	20.73
		36.50	0.30	0.55	5.99	2.17	2.37	25.12
	Al Der	30.73	0.29	0.54	6.30	2.01	2.78	18.81
		24.45	0.28	0.50	5.67	3.10	3.00	11.73

Table 4. Shows the total concentrations of the element lead in mg.kg^{-1} and the percentages of the presence of the Pb forms in the soil after addition

Governorate	Region	Total mg kg^{-1}	Soluble	Exchangeable	% binded with carbonate caco$_3$	% binded with organic mater OM	% binded with oxides OX	% Remaining in clay
Duhok	Amadiah	74.40	0.27	1.14	26.52	21.95	21.81	28.31
		71.92	0.40	1.38	33.20	14.25	15.13	35.64
	Acrah	81.89	0.43	1.07	28.45	6.64	23.75	39.74
		80.80	0.32	1.20	27.40	16.13	23.00	31.94
	Smell	75.61	0.30	0.83	28.91	16.80	22.64	30.51
		78.28	0.34	1.03	35.71	7.02	18.23	37.56
	Essaouira	77.88	0.42	0.99	41.58	9.60	4.40	43.00
		81.50	0.36	1.08	38.07	7.39	5.45	47.66
Wasit	Kut	82.37	0.46	0.83	32.18	8.86	11.50	46.99
		71.86	0.81	1.20	40.38	2.31	11.49	43.81
	Numania	76.58	0.62	1.20	36.77	10.41	4.82	46.28
		82.04	0.77	1.20	35.07	7.18	14.37	41.57
	Shirqat	79.36	0.86	1.18	18.81	7.91	23.31	47.92
		81.36	0.82	1.19	32.44	8.39	20.88	36.27
Salahaddin	Al Faris	71.72	0.82	1.28	25.92	8.05	5.56	58.37
		65.25	0.81	1.36	24.55	4.63	6.90	61.75
	Al Dur	57.79	1.04	1.51	24.57	6.80	6.94	59.15
		68.53	0.92	1.04	24.83	5.15	6.25	61.45
	Zubair	71.62	0.57	1.10	32.50	5.51	4.30	56.00
		62.20	0.64	1.17	32.93	5.26	5.16	54.84
Basra	Al Qarna	73.14	0.52	1.12	30.59	4.99	5.70	57.10
		76.50	0.46	1.12	22.08	4.59	3.93	67.83
	Al Der	70.73	0.51	1.09	36.25	4.38	5.12	5.65
		64.45	0.54	1.23	29.71	7.54	7.74	50.64

A significant positive relationship (*)was found with a coefficient of determination (R^2) = 0.22 for lead ions correlated with organic soil materials with the clay fraction relative to other soil components. Concerning the multiple correlation relationship, a highly significant positive relationship (**)was found with a coefficient of determination (R^2) = 0.52 for lead ions with the main soil components combined according to the following equation: - Since Y^= lead correlated with organic matter

Y^=3.42+0.00661X1-0.01066X2-0.00865X3+0.12587X4+0.52730X5+0.46630 X6

Most of the recent studies have directed their objectives towards the correlation of lead ions with organic soil materials as a serious attempt to reduce the danger and toxicity of this element by holding and retention it in the soil through its basic components that nature has endowed it with. Organic soil materials are considered an ideal and efficient cleaning agent with high efficiency and effectiveness and are environmentally friendly. It depends on several factors, including the quantity and quality of organic materials, the extent of their exposure to decomposition and oxidation, according to the surrounding environmental conditions, the soil system, the concentration and characteristics of the heavy element, the ionic strength, the soil reaction number, and the overall auxiliary conditions in the occurrence of both the processes of decomposition and oxidation such as the availability of water and temperatures. There is likely a high affinity and preference in the active sites of organic materials towards correlation with ions with positive double charges such as lead and cadmium, due to the high ionic exchange capacity of organic materials, and this was indicated by (5,9,24). The percentages of lead ions correlated to free iron oxides after addition ranged between (3.93-23.75)% of the total concentration of lead. These numbers constitute good percentages and they came in agreement with the soil content of total free iron oxides and amorphous oxides, which ranged between 0.07-5.26 $g.kg^{-1}$ and 0.02-0.08 $g.kg^{-1}$, respectively, in addition to the exposure of the soil to successive cycles of wetting and drying, which had encouraged the occurrence of each of the oxidation and reduction processes by providing the appropriate conditions for their occurrence, and then in the ratios of lead ions correlation to the oxides. As the oxides can excel in their adsorption of heavy elements from the rest of the other soil components if they are present in good quantities in the soil and under suitable conditions, and this is evident through the emergence of a highly significant positive relationship (**) for the lead ions correlated with the oxides with the soil content of free iron oxides percentage to the rest of the other soil components with a coefficient of determination (R^2) = 0.66 concerning the simple linear correlation coefficient. As for the multiple correlations, a highly significant positive relationship (**)was found with a coefficient of determination (R^2) = 0.72 for lead ions correlated with oxides with the main soil components combined according to the following equation: - Since Y ^ = lead correlated with free oxides of iron

Y^=3.58-0.0050486 X1+0.00300 X2-0.02123 X3+0.02148 X4+1.66924 X5+54.41838 X6

These results came close to what Al-Hilfi(10) and Taha et al (29) concluded, as the researcher found that lead ions correlated with free iron oxides formed (18.60-26.80)% of the total soil content of lead, according to the oxides contained in her study soils and the surrounding conditions. The correlation of lead ions with iron oxides will precipitate it in the soil environment in the form of various mineral compounds that are less dangerous than their correlation with organic soil materials, which in turn are also subject to decomposition and disintegration and then released back into the soil solution with the availability of appropriate conditions, as well as by increasing the wetting and drying cycles may have promoted to some degree the creation of additional conditions of alternating and continuous oxidation and reduction for the various iron-containing compounds in the soil. The percentages of lead ions remaining in the soil after addition ranged between (5.65-67.83)% of the total lead, as it was observed through the results that a clear discrepancy occurred in the percentages of the remaining lead ions in different soils, and this may reflect the extent of the effect of the quantity and quality of the dominant clay mineral. As smectite minerals prevailed in the soil samples obtained from the regions of Dohuk and Wasit, both Mica and Palygorskite minerals prevailed in the soils of Salah al-Din and Basra. The basic idea that was based on estimating the amount of the remaining element in the soil has focused mainly on the effectiveness of the clay fraction , being the colloidal part remaining in the soil that has the characteristic of adsorption and stabilization compared to the rest of the other soil fractions, due to its high surface area relative to the small size of its particles. An increase in the percentage of lead ions binded to the clay fraction was observed, and its superiority over the rest of the other soil components in some soils, since the clay fractions has a high surface area, which makes it more influential in most of the properties of the soil and nature of the effective chemical, physical and biological processes in the soil. A highly significant positive relationship (**) was found for the residual lead in the soil and the soil content of the clay fraction with a coefficient of determination (R^2) = 0.69, and a significant positive relationship (*) for the remaining lead in the soil with total iron oxides relative to the rest of the other soil components with a coefficient of determination (R^2) = 0.19, this is concerning the simple linear correlation. As for the multiple correlations, a significant positive relationship (*) was found for the lead with the main soil components combined with a coefficient of determination (R^2) = 0.25 according to the following equation: - Since Y^ = lead remaining in the soil

Y^=41.83-0.01056 X1+0.03945 X2-0.08005 X3+0.02925 X4+0.91363 X5+65.44751 X6

This is consistent with resultes of Ahmed and Abdul-Razzaq (3) and Tessier et .al (28)) they showed that lead ions in soils can enter into the crystal structure of some soil minerals, and then they will represent the most stable forms in soils, making them unavailable or accessible to plants. As for the influence of the dominant type of clay mineral, the results showed that the soils in which the mineral composition dominated smectite > mica > chlorite > kaolinite were more able to influence the lead content in the soil compared to soils that had a different mineral arrangement shows in Table **2**. This may be attributed to the role of these minerals in the fixation or adsorption of lead compared to other minerals (4). In general, lead is among the elements that are characterized by aggregation and accumulation in soils, due to its lack of movement, in addition to the fact that most of its compounds have a weak solubility in water, and it does not dissolve with irrigation water, and its solubility is greatly affected by the soil pH. Through the application of the statistical program in the prediction equations (prediction), a highly significant positive correlation (**) appeared for the total lead concentration with the various soil components. The highest of these was recorded with organic soil materials relative to the rest of the other soil components, with a coefficient of determination (R^2) = 0.34. This is concerning the simple linear correlation. As for the multiple correlations, a highly significant positive relationship (**) was found for the total lead concentration with the main soil components combined with a coefficient of determination (R^2) = 0.53 according to the following equation: - Since Y^= total lead

Y^=63.72 -0.00056X1+0.0358X2-0.0025X3+0.262X4+0.487X5+11.64X6

Sequential Extraction of Cadmium

Tables **5** and **6** show the different concentrations of cadmium ions binded with the different soil components before and after the addition, as the results showed that the percentages of the presence of soluble cadmium ions in the soil solution after the addition ranged between (0.49-1.66)% of the total concentration of cadmium. A significant positive correlation (*) was found for soluble cadmium with carbonate minerals relative to the rest of the other soil components and with a coefficient of determination (R^2) = 0.20, this is for the simple linear correlation. As for the multiple correlations, a non-significant relationship (NS) was found for soluble cadmium with soil components combined with a coefficient of determination (R^2) = 0.15 according to the following equation: Since Y^= soluble cadmium

Y^=0.30-0.00024362X1+0.00007417 X2+0.00139 X3+0.00275 X4+0.00468 X5-0.45539 X6

The percentages of the presence of exchangeable cadmium in the soil after addition ranged between (1.13-2.47)% of the total concentration, as a highly significant positive correlation (**)was found for the exchange cadmium with active lime with a coefficient of determination (R^2) = 0.34, this is for the simple linear correlation, but in the multiple correlations, the positive significant relationship (*) was found with a coefficient of determination (R^2) = (0.30) with the main soil components combined according to the following equation: - Since Y ^ = exchange cadmium

Y^=0.76+0.000202089X1-0.00012138 X2+0.00224 X3+0.00238 X4+0.00294 X5-0.51800 X6

This was confirmed by Al-Hassoun et al(7) who showed that a large part of the cadmium added tothe soil adsorbed on the surfaces of soil particles and was exchangeable. The correlation percentages of cadmium ions with carbonate minerals in the soil of the study after addition ranged between (40.74-79.51)% of the total concentration of cadmium. These percentages are high and at the same time, they are considered acceptable compared to the total soil content of the element and its binding to the other soil components. It is a good and healthy condition in the soil because it works to retain cadmium ions and restrict their movement and transfers in them, which reduces their toxic effects.Moreover, a highly significant positive correlation (**) was found for cadmium ions correlated with carbonate minerals with the soil content of active lime with a coefficient of determination (R^2) = 0.29. likewise, a significant correlation (*) was found for cadmium ions binded with carbonates with total iron oxides in the soil with a coefficient of determination (R^2) = 0.20, this is for the simple linear correlation, but in the multiple correlations, a highly significant positive relationship (**) was found for lead correlated with carbonates, with a coefficient of determination (R^2) = (0.61) with the main soil components combined according to the following equation. As Y^= is cadmium correlated with carbonate minerals.=

Y^=20.10+0.00151X1+0.00365 X2+0.07655 X3-0.00189 X4-1.11187 X5-14.53849 X6

The increase in the soil content of carbonate minerals will inevitably lead to a similar increase in the correlation rates of cadmium ions to carbonate minerals of all kinds due to the effect of the adsorption and precipitation processes occurring on their surfaces (10). Furthermore Zhao et al(32) showed that the increase in the rates of presence of the carbonates minerals in the soil will increase the adsorption and precipitation of cadmium ions in calcareous soils, as a relatively high affinity for cadmium ions to the active carbon surfaces was identified by the presence of deposits of $CdCO_3$ widely spread at these surfaces. Li et al(22) also showed that cadmium ions can bind strongly to the surfaces of carbonate minerals as a result of the high chemical affinity that these ions possess to carbon radicals, as a result of the great convergence between their radii, as the radius of the cadmium ion is (0.97 A^0). and the radius of the calcium ion (0.99 A^0).As the content of the study soil of carbonate minerals ranged between 48.2-363.5 $g.kg^{-1}$ soil, especially the calcite mineral, which constitutes the most present percentage in the Iraqi soils of a calcareous nature, and one of its most prominent characteristics is its high ability to adsorb many cations in the soil solution, including of the heavy element ions, as well as their content of active lime, ranged between 24-115 $g.kg^{-1}$ soil. Therefore, the most important characteristic of the study soils is the almost complete dominance of calcium and bicarbonate ions over the exchange complex. As for the correlation percentages of cadmium ions with organic soil materials in the soil solution after addition, they ranged between (0.24-7.98)% of the total concentration of cadmium. It is noticeable from the results consistency with the soil content of organic matter, which ranged between 0.7-36.2 $g.kg^{-1}$ soil. The organic soil materials are characterized by their high susceptibility to the adsorption of positive ions by making the surface more negative, and this correlation depends in its strength on the amount of ionization of the active groups possessed by the surfaces of the organic materials, which in turn will be affected by the pH of the medium directly and according to the pH of the study soils, which were within the range of 7.2-8.0 pH, it is considered by its nature to be neutral tending to weak basicity, so the process of adsorption of cadmium ions on to the surfaces of organic materials through its effective aggregates becomes very likely. This opinion was agreed with (9,17). It was also noted through the results the high efficiency shown by the organic soil materials in some of the study soils in their rapid adsorption of cadmium ions and then their complexity into complexes that have been subjected to different degrees of stability under the influence of the surrounding conditions and the soil content of those materials. Perhaps the reason for this is due to the presence of a relative affinity and preference for the surfaces of organic matter with cations, especially the divalent M^{+2} as a result of having a high ionic exchange capacity of 300 Cmol kg^{-1} organic matter (2). A highly significant positive correlation (**) for cadmium ions correlated with the organic matter with the soil content of organic matter with a coefficient of determination (R^2) = 0.67. It also a significant positive correlation (*) was found for cadmium ions correlated with the organic matter with the soil content of total oxides for iron relative to the rest of the other soil components, with a coefficient of determination (R^2) = 0.16, this is concerning the simple linear correlation, but in the multiple correlations, the highly positive significant relationship (**) was found for cadmium correlated with organic matter, with a coefficient of determination (R^2) = (0.77) with the main soil components combined according to the following equation:

Since Y^= is cadmium correlated with organic soil materials

Y^=0.02+0.000287X1-0.00174 X2+0.00014204 X3+0.09405 X4-0.17405 X5+17.88333 X6

The binding percentages of cadmium ions with free iron oxides in the study soil after addition ranged between (3.25-36.76)% of the total concentration of cadmium, as the total soil content of free iron oxides is very important in affecting the movement, adsorption, and precipitation of cadmium ions through its possession of influential chemical activity in all the reactions that take place in the soil as a result of its high surface area, and the degree of crystallization of these oxides is of great importance in that, and in general, the results were consistent with the soil content of total oxides and amorphous oxides. The type of bond that occurs between those free surfaces of oxides charged with negative charges and cadmium ions charged with positive charges, whether externally occurring at the surface or internally, was within the crystal structure of iron-bearing minerals. It mainly depends on the amount of relative affinity and preference between the polluting element and the surfaces of those oxides, the concentration of the heavy element, and the period of soil exposed to the pollutant, as well as the degree of crystallization of the oxides, this is consistent with (18). The exposure of the soil to successive cycles of wetting and drying inevitably encouraged an increase in the occurrence of both oxidation and reduction processes and thus affected the forms of iron and its release from its various compounds, which increased the chance of cadmium ions adsorped to the surfaces of these oxides. A highly significant positive correlation (**) was found of cadmium ions correlated with oxides with free total iron oxides in the soil with a coefficient of determination (R^2) = 0.70. However, a non-significant relationship (NS) was observed with each of the separate clay particles, total carbonate minerals, and active lime with a coefficient of determination (R^2) = 0.06, 0.02, 0.00, respectively

Table 5. Shows the total concentrations of the cadmium in mg.kg^{-1} and the percentages % of the presence of cadmium forms in the soil before addition

Governorate	Region	Total Mg kg^{-1}	Soluble	Exchangeable	% binded with Carbonate minerals $caco_3$	% binded with organic mater OM	% binded with oxides OX	% Remaining in clay
	Amadiah	1.58	0.01	0.02	0.73	0.00	0.17	0.56
		0.71	0.00	0.02	0.32	0.00	0.27	0.10
Duhok	Acrah	0.34	0.00	0.01	0.21	0.00	0.10	0.02
		0.43	0.00	0.02	0.22	0.00	0.13	0.02
	Smell	0.16	0.00	0.01	0.05	0.00	0.02	0.02
		0.57	0.00	0.02	0.39	0.00	0.13	0.03
	Essaouira	0.57	0.00	0.01	0.36	0.00	0.15	0.05
		0.65	0.00	0.01	0.41	0.00	0.18	0.05
Wasit	Kut	0.56	0.00	0.02	0.34	0.00	0.16	0.04
		0.50	0.00	0.01	0.36	0.00	0.03	0.10
	Numania	0.60	0.00	0.02	0.36	0.00	0.11	0.11
		0.52	0.00	0.02	0.30	0.00	0.10	0.10
	Shirqat	0.58	0.00	0.01	0.36	0.00	0.15	0.05
		0.58	0.00	0.01	0.41	0.00	0.18	0.05
Salahaddin	Al Faris	0.82	0.00	0.02	0.34	0.00	0.16	0.54
		1.05	0.00	0.01	0.36	0.00	0.03	0.49
	Al Dur	0.28	0.00	0.02	0.36	0.00	0.11	0.58
		1.19	0.00	0.02	0.30	0.00	0.10	0.05
	Zubair	1.60	0.00	0.03	0.96	0.00	0.20	0.33
		1.09	0.00	0.02	0.65	0.00	0.10	0.32
Basra	Al Qarna	1.40	0.00	0.04	0.75	0.00	0.18	0.33
		1.61	0.00	0.04	0.96	0.00	0.16	0.46
	Al Der	0.91	0.00	0.02	0.52	0.00	0.09	0.28
		0.86	0.00	0.02	0.55	0.00	0.07	0.24

Table 6. Shows the total concentrations of cadmium in mg.kg^{-1} and the percentages % of the presence of cadmium forms in the soil after addition

Governorate	Region	Total Mg kg^{-1}	Soluble	Exchangeable	% binded with Carbonate minerals $caco_3$	% binded with organic materOM	% binded with oxides OX	% Remaining in clay
	Amadiah	41.58	1.64	2.26	40.74	7.98	32.08	15.26
		40.71	1.66	2.36	51.88	2.70	30.10	10.40
Duhok	Acrah	40.34	0.67	1.69	43.83	10.01	36.76	6.74
		40.43	0.87	1.66	47.10	5.31	35.91	9.15
	Smell	40.16	0.87	2.47	47.61	4.58	33.44	11.03
		40.57	0.94	2.32	52.06	0.44	32.66	11.58
	Essaouira	40.57	0.92	2.07	76.73	5.23	4.04	10.57
		40.65	0.64	2.31	75.99	1.87	6.17	13.01
Wasit	Kut	40.56	1.33	2.34	69.01	4.93	13.66	8.73
		40.50	1.36	1.93	69.93	7.38	11.36	8.05
	Numanism	40.60	1.11	1.93	79.51	1.30	5.71	10.47
		40.52	0.27	1.95	75.89	0.49	11.41	5.13
	Shirqat	40.58	0.86	1.87	76.67	3.60	35.85	11.16
		40.58	0.94	2.27	51.23	4.16	34.25	7.05
Salahaddin	Al Faris	40.82	1.03	2.08	52.16	0.49	6.00	38.24
		41.05	0.97	53.74	53.74	0.24	8.77	34.03
	Al Dur	40.28	0.79	2.31	60.30	0.45	9.33	29.29
		41.19	0.75	2.16	58.12	0.39	8.96	29.62
	Zubair	41.60	0.63	2.14	53.10	5.31	10.34	28.94
		41.09	0.66	1.99	55.05	1.95	10.54	29.79
Basra	Al Qarna	41.40	0.68	1.57	55.17	3.33	11.78	27.46
		41.61	0.70	1.13	52.22	2.38	9.88	33.69
	Al Der	40.91	0.49	1.83	54.44	1.47	11.66	30.11
		40.86	0.64	1.40	52.74	4.87	13.83	26.82

This is concerning the simple linear correlation, but in the multiple, the positive highly significant relationship (**) was found with a coefficient of determination (R^2) = 0.76 with the main soil components combined according to the following equation: - Since Y^= cadmium correlated with free iron oxides Y^=3.11-0.00048230 X1+0.000801 X2-0.02256 X3+0.2610 X4+1.45928 X5+53.32934 X6

This is consistent with Ahmed et al. (3) and Al-Zubaidi (17) who showed that the total soil content of free iron oxides is very important in affecting the movement, adsorption, and precipitation of cadmium ions through the chemical activity they possess in the soil because of the high surface area of these oxides possess, the researcher concluded that Cd^{+2} cadmium ions may show a tendency of different degrees of intensity to bind with the negative charges available on the surfaces of these oxides in the soil. The percentages of cadmium ions binded to the clay fraction in the study soil after addition ranged between (6.74-38.24)% of the total concentration of cadmium. At this stage of the sequential extraction processes, the effectiveness of the clay particles appears in the soil, as it may be the effective colloidal part remaining in it compared to the rest of the other soil fraction such as silt and sand, which has an adsorption characteristic, and here its great importance appears in determining an important number of chemical and physical characteristics in different types of soils. It was observed through the results that there was a variance in the ratios of cadmium ions binding to the surfaces of the clay particles as a result of the variation in the mineral composition and the presence and dominance of different minerals in the study soils. As the relative decrease in the amount of cadmium associated with the clay fraction in some of the study soils, although this fraction has a high surface area with a predominance of highly charged smectite minerals, which in turn possesses a high ionic exchange capacity within the study clays. It can be attributed to the presence of a large state of competition between calcium ions and cadmium ions present in the soil solution in an attempt to occupy most of the exchange sites on the surfaces of the clay fraction (this means the appearance of the accompanying ion state), and that this competition process will be controlled by both the ion radius and its concentration in the soil solution, as the cadmium ion has a radius of 0.97 A^0, which is of course close to the radius of the calcium ion of 0.99 A^0, which has facilitated the ion exchange process and then the distribution and occupancy of those sites between them. But because of the nature of the parent materials of the Iraqi calcareous soil in which calcium ions predominate in abundance, it will make high concentrations of calcium ions occupy most of the sites by outperforming the cadmium ions in the soil solution, which facilitates the displacement of part of the cadmium ions from most of the surfaces of those exchange sites. That is, the case of the relative dominance of the effect of ion concentration appears here in the success of the competition and control process over the majority of sites, which has led to a relative decrease in the rates of the cadmium ions fraction to the surfaces of the clay in some of the study soils, and then an increase in their movement in the soil. As well as, by expanding the scope of the horizon, this situation can be viewed from another side and interpreted according to the principle that the variation in the rates of binding cadmium with the separate clay particles may be attributed to the differences like the form in which the carbonate minerals were found in those soils, which worked on encapsulating most of the clay particles, which affected the efficiency of its adsorption of cadmium ions or may be due to its closure of a large part of the ion exchange sites, which impeded the occurrence of adsorption processes on the surfaces of clay particles through the formation of coating films or covers of free iron oxides. Also, the domination of smectite minerals in most of the study soils had a positive effect on the soil through the retention of these minerals to a large part of the cadmium ions added to the soil solution (23). A highly significant positive correlation (**) was found for cadmium ions correlated with clay particles (remaining in the soil) with all soil components individually and recorded the highest with the soil content of active lime wit a coefficient of determination (R^2) = 0.49 concerning the simple linear correlation, as for the multiple correlations, the highly significant relationship (**)was found for the remaining cadmium ions in the soil with a coefficient of determination (R^2) = 0.89 with the main soil components combined according to the following equation: - Since Y^= cadmium correlated with clay (remaining in the soil)

Y^=16.49-0.000864 X1-0.00467 X2 -0.5485 X3-120.77 X4-0.31789 X5-40.90551 X6

As for the effect of the clay mineral type on the behavior of cadmium in soils, the soils were of mineral order Palygorskite > mica > chlorite > smectite> kaolinite are the most influential as compared to other forms as shown in Table 2. The concentrations of total cadmium ions in the study soil after the addition ranged between (40.16-41.61) mg.kg^{-1} which in general has exceeded the internationally allowed critical limits in all soils, amounting to 3 mg.kg^{-1} soil according (30), which shows that all soils have become heavily contaminated with this element after addition, as cadmium was added to all soils at a concentration of 40 mg.kg^{-1} to achieve one of the most important objectives of the study, which is tracking the physiochemical path of cadmium ions in different soils as an attempt to limit or reduce its movement in soils, which contributes in one way or another to reduce its harmful effects on the environment.

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