

STUDY OF THE MINERAL COMPOSITION OF SOME IRAQI SOILS AND ITS EFFECT ON ZINC ADSORPTION

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Abstract

Nine sites were selected representing eight governorates with varying climatic conditions (Jawar Qornah village S1/ Sulaymaniyah governorate, Tawqq S2/Erbil, Zawiya S3/Dohuk, Abu Ghraib S4 and Mahmudiya district S5/ Baghdad, Khan Bani Saad S6 / Diyala governorate, Hamrannan S7/ Basra governorate and Batha /S8 Dhi Qarloqat governorate, Saleh Castle S9/Maysan governorate) to study the mineral composition of some Iraqi soils and its effect on zinc adsorption. The results of X-ray diffraction curves showed that the nature of the clay minerals diagnosed varied according to the study soil, and that the clay minerals appeared in the following order: Muscovite > pialgrosscite > Montmorlite > Chlorite > Kaolinite at sites S2, S5 and S7, while at S6, they were Moscovite > Montmorillonite > paligrosscite > Chlorite > Kaolinite, whereas Moscovite > Clorite > paligrosscite > Chlorite > Kaolinite > chlorite at site S8, while in Moscovite order > montmorelite > chlorite > Kaolinite at site S4, chlorite > Moscovite > paligorskite > Kaolinite sequentially at sites S1 and S3, the results also showed the presence of irregular applicable metal Mica-Chlorite at both sites S1 and S9. The adsorption experiment was carried out using the Langmure equation to describe the adsorption process of zinc on the study soil. The results showed that the maximum adsorption values and binding energy were different from one location to another due to the difference in the content of the clay soils and the ratio of the montmorillonite and chlorite minerals compared to the other existing minerals. The maximum adsorption values were 555.5, 400.0, 344.8, 526.3, 384.6, 434.7 and 454. 0, 500.0 and 322.5 μ gZn g⁻¹ soil, and the binding energy values were 0.90, 1.92, 1.38, 2.11, 0.66, 1.91, 1.22, 1.66 and 1.93 ml μ g⁻¹Zn for soil S1 to S9 respectively.

Key words: calcareous soils, clay minerals, mineral analysis, zinc adsorption.

Introduction

The clay plays an active role in determining the physical and chemical properties of the soil It is involved in electrochemical reactions such as ion exchange and ion stabilization as a result of having a superficial charge. The mud is also characterized by its large surface area and effective and has the ability to retain water and the ability to swell and shrinkage due to the process of expansion as well as has a high regulatory capacity

clay is exposed as the rest of the soil components Transformation due to weathering conditions due to climatic factors and the change in soil reaction, resulting in new clay minerals (Newman, 1984). The distribution of clay minerals or their relative presence in the soil varies depending on the soil composition factors. Soil minerals inherited from the parent material go through transformation stages over time and by responding to

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weathering conditions (Niederbudde and Fisher, 1980),

It is noted that there are differences in the prevalence of certain types of clay minerals with differing climatic conditions. Al-Huwaizi (1995) stated that the formation of secondary minerals and the geochemical transformation of primary minerals depends mainly on the movement of cations in the weathering area, and they added that the fluctuation in the ground water level and increasing the concentration of magnesium in the soil and ground water leads to the sovereignty of the Cemiktiat mineral in the soil. Saleh (2018) stated that regional variations in annual rainfall play a key role in determining the quantity and quality of clay minerals prevalent in each region. Many chemical reactions such as cation exchange, adsorption and release of elements depend on the type and amount of clay minerals in the soil (Khatib, 2006).

Aljdou (1990) showed a significant positive correlation between the total content of zinc and the content of clay in soil and added that the montmorillonite and chlorite minerals have high susceptibility to the adsorption and stabilization of zinc between their crystalline layers. Akay and Doulati (2012) pointed out that the soil content of clay And clay mineral type Play an active role in the adsorption of zinc in the soil and they added that the clay minerals as Mica , Illite , chlorite and Simectite characterized by high ability on the adsorption of zinc being of 1 : 2 and 1 : 2 : 1 minerals. The aim of this research is to study the mineral composition of zinc.

Materials and methods

Soil samples were collected from eight different governorates in climatic conditions in terms of rainfall, temperature and intensity of weathering. The sample was taken from the surface layer of the soil at a depth of 0-30 cm and dried pneumatically, grinded and passed through a sieve with a 2 mm diameter. The required physical, chemical and metallic analyzes were carried out according to the methods in Bashour and Al-Sayegh (2007). Table 2 shows some of the chemical and physical properties of the study soil. Total zinc was determined by wet oxidation using H_2SO_4 , HNO₃ and HCl acids as reported in Page *et al.*, (1982).

X-ray diffraction examination

Used clay samples from which all binders were removed and saturated with magnesium and potassium. Glass slides were prepared and allowed to air dry according to Theisen and Harward (1962). Ethylene glycol was treated for magnesium saturated slices to detect the presence of expanded minerals by a 10% solution of glycol according to the Jackson method (1979). Heated Potassium saturated slices after tested at 25 ° C for 2 hours and 350 and 550°C were examined after each heating phase to determine the nature of clay minerals in each sample. The percentage of clay minerals for the samples diagnosed was calculated by measuring the area under curve in a semi-quantitative manner and based on the thickness of the mineral layer (d-spacing) (Gjems, 1967).

Zinc adsorption experiment

The adsorption experiment was carried out on the soil samples after removal the cementation agent and treating it with five concentrations of zinc (0, 10, 20, 30 and 40 micrograms Zn g soil ⁻¹). The maximum adsorption values(Xm) and binding energy(k) were calculated by applying the Langmuir equation:

As:

C = ion concentration measured in equilibrium solution

 $(\mu g Zn g^{-1} soil)$

- x = adsorbed ion concentration per unit weight of soil (µg Zn g⁻¹ soil)
- Xm= constant equation and expresses the maximum adsorption of the ion (μ g Zn g⁻¹ soil)
- k = constant of the equation and expresses the binding energy (ml µg ⁻¹).

Results and Discussion

X-ray diffraction examination

The results of X-ray diffraction curves (Figures 1, 2, 3, 4, 5, 6, 7, 8 and 9) show the following:- The appearance of 14.49 A° at sites S1, S3 and S5, 14A° at S2, 13.81 A° at S4, 14.4 A° at S6 and S7, 14.2 A° at S8 and 14.03 A° at S9 in magnesium and dry aerobic treatment are consistent with the presence and persistence of treatments, Indicates the presence of real chlorite metal resistant to heat, and this is consistent with the findings of Jarallah and Isa (2012).

- The presence of diffraction 13.81 A° at site S4 in the treatment of magnesium saturation and aerobic dry and the widening of its basal distance to 17.67 A° in the treatment of ethylene glycol saturation and disappearance when heating treatment to 350°C, the diffraction 14.49 A° at site S5 in magnesium-aerobic drying and aerobic drying and then widened to 16.36 A° in ethylene-glycol saturation, diffraction 14.4 A° at sites S6 and S7 in magnesium and aerobic dry saturation and then widened to 18.41 A° in ethylene glycol saturation, 14.2 A° at site S8 in magnesium and dry saturation The basal distance to 15.78 A° in the saturation treatment of ethylene glycol and its disappearance in the heating treatment to 350°C confirms the presence of the monmononalite mineral, which is consistent with Jubouri's findings (2010).
- The appearance of 10.5 A° diffraction at sites S1, S2 and S3, and 10.51 A° diffraction at sites S5, S6, S7, S8 and S9 in the treatment of magnesium saturation and aerodynamic dryness indicate the presence of palligorskite mineral, and this result is consistent with the findings of the al-Dahi (2009).
- The appearance of diffraction at basal distance 14.49 A° at site S2 in magnesium saturated and aerobically dry treatment and then widened to 16.67 A° in ethylene glycol saturation treatment and then returned to 10.16 A° in potassium saturation and heated to 350°C indicates the presence of montmorillonite mineral, and the high intensity of diffraction 10.16 A° at the expense of diffraction intensity of 14.49 A° within the potassium saturation and heated treatment to a temperature of

Property	unit	Governorates								
		S1	S2	S3	S4	S5	S6	S7	S8	S9
Texture		C.L	Si.C.L	Si.L	C.L	Si.C.L	Si.L	C.L	Si.C.L	Si.L
Sand	gm.kg ⁻¹	398	200	264	396	165	214	404	190	215
Silt		192	430	526	182	475	546	186	460	535
Clay		410	370	210	422	360	238	410	350	250
EC	dS.m ⁻¹	0.40	0.80	0.63	2.72	1.83	2.74	4.40	6.60	5.60
CEC	Cmol ckg ⁻¹	26.6	21.3	16.5	24.7	21.6	16.4	21.3	19.0	16.3
O.M	%	1.33	1.28	1.23	1.18	1.02	1.10	0.88	0.97	0.78
Total Carbonate	gm.kg ⁻¹	40.2	44.0	44.8	243.0	240.0	211.0	298.0	357.0	334.0
Active lime		35.4	39.6	41.5	191.0	182.0	152.0	196.0	251.0	228.0
pН		7.0	7.1	7.0	7.6	7.5	7.4	8.0	8.2	7.9
Total Zn	gm.kg ⁻¹	103.21	92.84	83.57	70.78	76.10	79.72	67.93	63.64	66.15
Available Zn		1.5528	1.3266	0.8696	0.7020	0.7126	0.7478	0.6924	0.5278	0.6538
Ca ⁺	mmol.l ⁻¹	2.01	4.01	3.00	6.45	4.80	5.76	9.13	12.72	11.83
Mg ⁺²		1.00	2.50	2.01	4.81	3.08	4.14	5.67	10.45	6.41
Na ⁺		0.90	1.22	1.18	4.73	1.33	6.82	13.78	20.13	19.60
K ⁺		0.31	0.51	0.40	0.90	0.71	0.90	0.70	0.20	0.41
Cl		2.21	4.81	4.16	23.06	15.63	23.21	15.09	28.46	18.84
SO_4^{-2}		1.13	1.11	1.03	1.25	0.53	0.80	10.64	13.25	12.73
HCO ₃ ⁻¹		1.40	1.41	1.60	1.80	0.88	1.20	8.78	11.14	12.60
CO ₃ -2		Nill	Nill	Nill	Nill	Nill	Nill	Nill	Nill	Nill

Table 2: Some chemical and physical properties of the study soil.

350°C confirms that monomolonite mineral is inherited from mica mineral.

- The appearance of 10.04 A° at S1 and S3, 10.1 A° at S2, S6, S7 and S8, 10.2 A° at S4 and S9, and 10.16 A° at S5, and the fact that it remains constant in all treatments indicates the presence of mica mineral in the sample, and that the appearance of the second mineral diffraction at the base distance 5 Highly indicative of the presence of the mineral mica dioctahydra (Moscuvite mineral).
- The appearance of 7.13 A° at S1, S3 and S4 and 7.19 A° at S2 and S5 and at 7.30 A° at S6, S7 and S8 and at 7.1 A° at S9 in magnesium and aerobic drying, and then disappearance in the treatment of potassium and heated saturation to 550°C indicates the presence of kaolinite, and this finding is consistent with the findings of Jarallah and Issa (2016).
- The appearance of 11.94 A° diffraction at site S1 and 12.4 A° diffraction at site S9 in magnesium-aerobically saturated and dry treatment indicates the presence of irregularly applied mica-chlorite, which is consistent with the Al-Gaf finding (2006).

The results of X-ray diffraction curves (Figures 1, 2, 3, 4, 5, 6, 7, 8, 9) and Table 3 show the following :

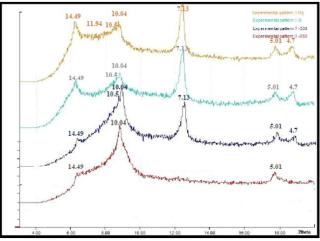
- The difference in the proportions of clay minerals that were diagnosed according to the study soils, It is

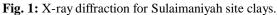
difficult to determine its cause; as a result of the occurrence of two phenomena in these minerals are Chloritization and Vermiculitization and cause transitions (Dreher, 1997).

- The emergence of moscovite, palegorskite, montmorillonite, chlorite and kaolinite sequentially at sites S2, S5 and S7.
- Presence of moscovite, montmorillonite, palegorskite, chlorite and kaolinite respectively at S6.
- The emergence of chlorite, moscovite, palegorskite and kaolinite minerals respectively at sites S1 and S3.
- Presence of palegorskite Moscovite then montmorillonite, kaolinite and chlorite minerals sequentially at site S9.
- The presence of palegorskite, moscovite, and then montmorillonite ,chlorite and kaolinite respectively at the site S8.
- The presence of palegorskite, mesquite and then montmorillonite valcaluminite and chlorite respectively at the site S8.
- The presence of moscovite, montmorillonite, chlorite and kaolinite minerals sequentially at site S4.
- Mica-chlorite irregular applied mineral was diagnosed at sites S1 and S9.
- The presence of montmolite in the study soil may be

due to the suitability of the chemical conditions prevailing in the study soil, which is characterized by the degree of base interaction with the full dominance of calcium and magnesium ions (Hanna, 1961).

- The presence of kaolinite in all sites at low rates may be attributed to the fact that the composition of this





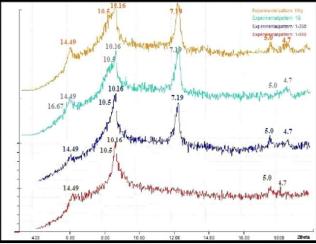


Fig. 2: X-ray diffraction of the site clays Erbil.

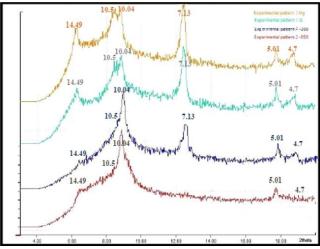
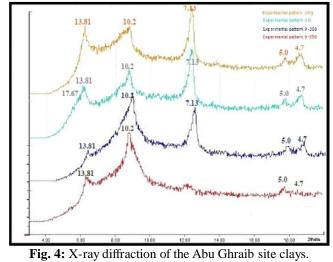


Fig. 3: X-ray diffraction of the Dohuk site clays.

mineral is not available in Iraqi soils, because it needs to severe washing conditions and soil reaction of soil tends to acidic with a very low concentration of bases such as calcium and magnesium on the exchange complex (Buol *et al.*, 1973) His presence may be the result of weathering, particularly the physicality of



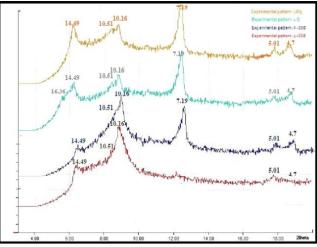


Fig. 5: X-ray diffraction of tangerine site clays.

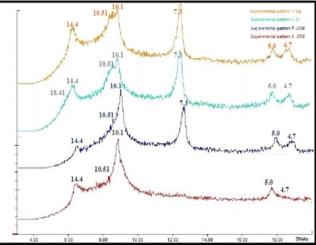
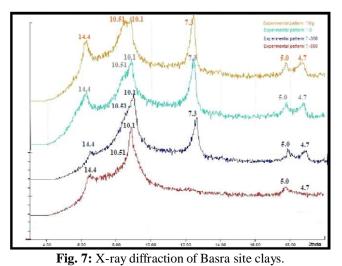
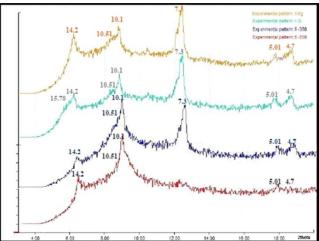


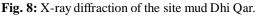
Fig. 6: X-ray diffraction for Diyala site clays.

smectite minerals, or due to his relocation (El Bakri, 1997).

- The main source of chlorite mineral in the study soil is the parent material, and there is a possibility of the metal formation from weathering mica in sedimentary soil, as the displacement of potassium by magnesium







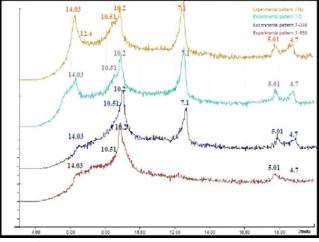


Fig. 9: X-ray diffraction of the Missan site clays.

found in the base environment of these soils lead to the formation of secondary minerals, or is formed as a result of the transformation of applied minerals such as chlorite - Smectite and chlorite-mica or that occurrence of the phenomenon of Chloritization, which is the transformation of smectite to chlorite by the deposition of magnesium oxides within the inter layers of the Smectite led to the presence of chlorite mineral

 Table 3: Percentages of clay minerals diagnosed in the study soils.

Site	Type of Mineral									
	Mon	Pal	Ms	Kaa	Chl					
S1	-	12.26	34.40	8.15	45.20					
S2	10.27	19.05	49.19	6.15	15.35					
S3	-	28.04	35.51	6.26	30.19					
S4	29.69	-	34.88	16.70	18.73					
S5	21.54	27.31	27.88	9.81	13.46					
S6	23.39	21.71	35.80	6.55	12.54					
S7	20.79	21.46	39.57	8.20	9.98					
S8	20.43	30.14	26.83	11.49	11.11					
S9	-	23.05	30.60	16.51	29.84					

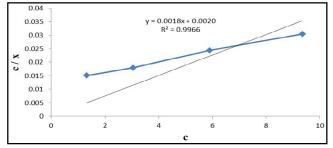


Fig. 10: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S1 soil.

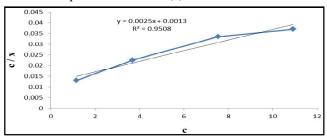


Fig. 11: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S2 soil.

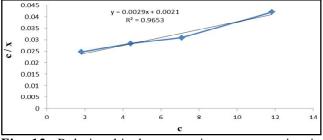


Fig. 12: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S3 soil.

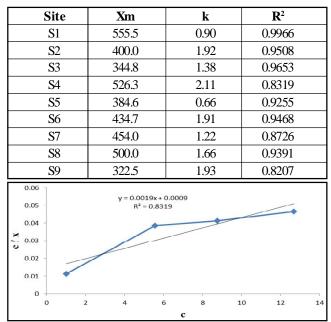


Table 4: Maximum adsorption values Xm (µg Zn g⁻¹ soil) and binding energy k (mlµg Zn).

Fig. 13: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S4 soil.

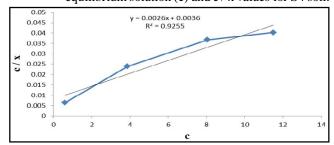


Fig. 14: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S5 soil.

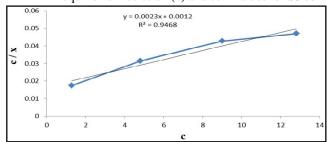


Fig. 15: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S6 soil.

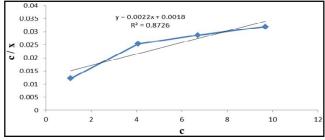
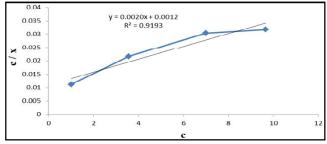
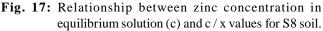
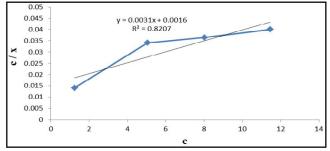
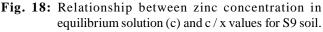


Fig. 16: Relationship between zinc concentration in equilibrium solution (c) and c / x values for S7 soil.









(Jackson, 1963).

The effect of mineral composition on the maximum adsorption values of Zinc and binding energy

The results of Figures 10-18 and Table 4 show the effect of mineral composition on the maximum adsorption values and binding energy. The maximum adsorption values(Xm) calculated from the application of Langmure equation were 555.5, 400.0 and 344.8 μ g Zn g⁻¹ soil with an average of 433.4µg Zn g⁻¹ soil and a binding energy of 0.90 1.92 and 1.38 ml µg Zn g⁻¹soil with an average of 1.40µg Zn g⁻¹soil in soil of the northern sites S1, S2 and S3 respectively, while 526.3, 384.6 and 434.7 µg Zn g ¹soil with an average of 448.5 µg Zn g⁻¹ soil and a binding energy of 2.11 and 0.66 And 1.91 µg Zn g⁻¹ soil with an average of 1.56 µg Zn g⁻¹ soil in soils of middle sites S4, S5 and S6, respectively, while their values were 454.0 and 500.0. The 322.5 μ g Zn g⁻¹ soil with an average 425.5 μ g Zn g⁻¹ soil with a binding energy of 1.22, 1.66 and 1.93 mcg-mlµg Zn g⁻¹soi1 an average of 1.60 mlµg Zn in the soil of the southern sites S7, S8 and S9 sequentially.

The above results show that the maximum adsorption values of zinc and binding energy varied from one location to another. This difference may be due to the variation of clay soil content (Table 2) and the type of clay minerals, particularly montmorillonite and chlorite (Figures 1-9 and Table 3).

These results are consistent with the findings Dahiya *et al.*, (2005), who noted that clay minerals and their type play an important role in determining the adsorbed

quantities of microelements, are also consistent with Jadou '(1990) which indicated that montmorillonite and chlorite minerals are highly adsorbent and stabilize Zinc between their layers. Crystalline, The montmorillonite mineral provides permanent negative charges on its surfaces, which increases its susceptibility to adsorption Especially since the montmorillonite in Iraqi soil is generally highly charged it has high adsorption sites and many due to the isomorphas substitution process in the tetrahydra and octahedra layers of the mineral, as well as the high charge on its surfaces has been inherited from the mica (Jabouri, 2010), as well as the results obtained in the present study which show that when examining montmorillonite diffraction (14A°) and mica diffraction (10A°) in the treatment of magnesium saturation and aerodynamic drying and comparing this In the treatment of potassium saturation and heated to 350°C, the diffraction intensity increased to 10A° at the expense of diffraction intensity of 14A° due to montmorillonite, This proves that montmorillonite in the soil under study is inherited from mica minerals with high surface charge, as well as other properties of montmorillonite such as its high surface area, all these reasons led to increased mineral susceptibility to Zinc adsorption on its surfaces, especially at sites S4 S7, whose soil contained a high content of clay, as well as the high clay content of montmorillonite.

As for chlorite, studies have shown that there is an inner hydroxide layer within the crystal structure of chlorite which is a 1 : 1 : 2 mineral. Hidroxid inner layer lead to high adsorption of micronutrients including zinc (Akay and Doulati, 2012), especially at the site S1, which the soil contained high percentage of clay, as well as the high proportion of chlorite in the clay and the disappearance of montmorillonite mineral, In this regard, Dixon et al., (1962) stated that the inner hydroxide layer is a trap for all elements, including Zinc. As for the sites S3 and S9, it is noted from the results that these sites recorded the lowest values of maximum adsorption after the removal of carbonate minerals, which may be attributed to the reduction of clay in the soil of these sites (Table 2) and the disappearance of montmorillonite (Table 3). As for the S5 site, the results showed that it had the lowest maximum adsorption value compared to S4 and S6 (middle sites), This may be attributed to the lower montmorillonite content in clay compared to the other two sites.

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