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Original Research

Studying the relationship between sodium adsorption ratio and exchangeable sodium percentage, and some thermodynamic parameters in the affected and non-affected soils with salts in Dhi Qar Province, Southern Iraq

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ABSTRACT:

A laboratory experiment was conducted according to the Completely Randomized Design (CRD) to study the relationship between (Sodium Adsorption Ratio and Exchangeable Sodium Percentage) and some thermodynamic parameters in the affected and non-affected soils with salts in Dhi Qar Province of Southern Iraq. The study included the selection of 21 soil samples representing seven locations, three soil samples took from different places for each location. To achieve this study, some conventional and thermodynamic calculations were required. The results showed very high concentrations of soluble sodium in the soils affected with salts range 141-755 mmol cal.L^{-1} compared to 0.03 mmol cal.L^{-1} in the soils non-affected with salts. sodium formed a ratio ranged from (0.002-0.009 and 0.31-0.75) to the sum of positive ions in the normal soils affected by salts, respectively. In the calculation of the thermodynamic parameters for sodium status evaluation, the ionic effectiveness treatment of sodium in the soils ranged from 0.02-24.77 and in the soils affected with salts from 31.3-60.1. Ionic effectiveness values ranged from 0.8-873.2 mmol cal.L^{-1} and 100-978 mmol cal.L^{-1} in non-saline soils and soils affected with salts respectively.

Keywords:

SAR, ESP, Non-saline soils, Saline soils.

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INTRODUCTION

Studies on ion exchange interactions have gained considerable importance at the beginning of the 20th century (Sposito and Mattigod, 1979). It is indicated that the application of chemical thermodynamics in soil systems has made an excellent effort to understand the equilibrium relationships between ionic species in soil solution and solid soil phase and this interest has continued to this day. In order to understand cation exchange interactions it is to be understood that this reaction is relatively quick and inverse when ion adsorption is on the surface of the solid phase. (Sumne and Miller, 1996). It is indicated that the ionic preference study is focused on describing the positive ionic structure of the solid soil phase, which is key to soils management. The study of sodium is important in determining the physical properties of semi-dry and irrigated soils with the expectation of dispersion, Beckett (1964) and Al-Kanani *et al*. (1989) indicated that the importance of the study of thermonuclear ion exchange is to identify the amount of ions in the solid soil phase and its intensity in the liquid soil phase. The extent of applying of this concept depends on the reciprocal traits of the soil components. The retention of ions and their release into the soil and plant solution slowly is one of the most important characteristics of some soils. Due to the importance of cation exchange interactions in the soil and its role in reducing nutrient loss during weathering and supplying plant with it, great efforts have been devoted to studying the nature of these reactions and their characteristics and the mathematical relations that describe the state of equilibrium that governs the process of cations exchange. In order to identify the effect of many factors on ion exchange such as quality of irrigation water, weathering and fertilization, it is necessary to investigate the type of cations exchanged, which are in balance with the new additions. The exchanged cations can give a clear picture about element deficiencies and degree of element toxicity and their role in the differentiation of soil and can be predicted all these effects and different levels of accuracy through the equations of cation exchange and using various theoretical and experimental approaches, The studies of cation exchange in modern Iraqi soil began with Seilsepour (2009). Which taught that the theory of the ion exchange of the Donan world was taken as a basis for deriving an equation by which the ratio of sodium exchange in the Iraqi soil could be measured. In recent years, the danger of salinity has begun to spread out into the southern regions, including Dhi Qar province, where most of the territory of Iraq is located in the dry and semi-dry regions, which depend on irrigated agriculture and that 75% of these lands according to what finding (Abdul-Qadir and Benni, 2010). It is influenced by different degrees of salinity, therefore, the need for a study of the properties of reactions in the systems containing sodium, calcium and magnesium and their trends in some of the soil of Dhi Qar province and nearby areas have revealed the validity of the use of the Capon equation and other equations through comparing between them using some statistical concepts in this field.

The objectives of the research are limited to the development of salty or sodic soils when irrigating with salt water, and to study the dependence coefficient (Gapon constant) for soils between sodium ion, calcium and magnesium. Also study on the effect of ionic strength. Ionic efficiency and some thermodynamic parameters of the soil were carried out.

MATERIALS AND METHODS

Collection and preparation of soils samples

A laboratory experiment was conducted in the laboratories of college of Agriculture, Sumer University using Complete Randomized Design (CRD) to study the relationship between SAR and ESP and some thermodynamic parameters in the affected and non-affected soils with salts in Dhi Qar Province, Southern Iraq. The soil samples were collected from different locations repre-

Table 1. Chemical and physical traits of non-saline soils

Sample number	Locations	pH	Salinity EC ds.m[1]	Calcite $g.kg^{-1}$	Organic matter $g.kg^{-1}$	Exchange capacity of positive ions $cmol.kg^{-1}$	Soil separates $g.kg^{-1}$			
							Sand	Silt	Clay	Texture
1	Fajar 3	7.8	2.72	217.1	16.8	27.13	410	310	280	Silty clayloam
2	Nasr 1	7.8	2.05	167.4	23.3	36.08	300	110	590	Clay
3	Rifai 3	7.6	4.47	236.4	18.9	22.12	410	360	230	loam
4	Shatrah 1	7.9	1.9	221.0	8.5	29.04	410	280	310	loam
5	Shatrah 2	8.2	0.26	217.9	15.8	30.13	280	400	320	loam
6	Shatrah 3	7.8	0.03	339.5	20.2	25.08	430	300	270	loam
7	Suq Al-Shuyukh 1	7.6	0.07	172.5	13.7	40.13	260	260	480	Clay loam
8	Suq Al-Shuyukh 2	7.8	0.13	269.8	12.7	41.17	360	120	520	Clay loam
9	Suq Al-Shuyukh 3	7.8	0.02	298.4	11.0	20.10	400	400	200	loam
10	Nasiriyah 1	7.7	0.30	233.8	14.4	20.35	610	185	205	sand clay loam
11	Nasiriyah 2	7.9	0.08	217.6	13.0	35.21	270	410	320	loam
12	Nasiriyah 3	7.8	0.07	258.9	21.3	30.17	710	100	190	Sand loam
LSD	0.823	0.016	3.12	0.823	0.823	4.12	4.12	4.12	0.823	

senting seven agricultural locations and non-agricultural locations in Dhi Qar Province.

Twenty one samples were collected from which, the soil samples were taken from the surface layers (0-30 cm) of these soils to represent locations samples. The samples were dried aerobically, sieved with a 2 mm sieve, then mixed well and stored inside plastic containers for the necessary analysis. Table 1 and 2 indicate some physical and chemical properties.

Thermodynamic parameters of sodium in the liquid soil phase

Ionic strength

The ionic strength of the soil solution and equilibrium solution was calculated according to the equation given by Griffin and Jurinak (1973):

I=0.013EC .... (1)

Where I = ionic strength $mol.L^{-1}$

EC = Electrical conductivity of the equilibrium solution $ds.m^{-1}$

Effectiveness coefficient of sodium ions

The effectiveness coefficient of sodium ion was calculated in soil solutions and equilibrium solutions

$$-\log f_{Na} = \frac{0.509 Zi^2 \sqrt{I}}{1+\sqrt{I}} - 0.3I \qquad (2)$$

according to Davis equation, which is contained in Sposito (1989).

Where $-\log f_{Na}$ expresses the negative logarithm of the Effectiveness coefficient of sodium ions

Zi^2: square charge ion.

Sodium ionic effectiveness

The sodium effectiveness was calculated according to the following equation:

a = c . f_i …………………..… (3)

a = Sodium effectiveness

c = sodium ion concentration

f_i = sodium effectiveness coefficient

Estimation of Gapon constant

A stable and calm equilibrium was performed using water in the ratio of: soil 1:10 for surface soil and then sodium in leachate using flame photometer, calcium and magnesium were estimated in EDSA while soil was extracted after equilibrium with 1 molar solution of ammonium acetate to estimate ions (sodium, calcium

Table 2. Chemical and physical traits of saline soils

Sample number	Locations	pH	Salinity EC $ds.m^{-1}$	Calcite $g.kg^{-1}$	Organic matter $g.kg^{-1}$	Exchange capacity of positive ions $cmol.kg^{-1}$	Soil separates $g.kg^{-1}$			
							Sand	Silt	Clay	Texture
13	Fajar 3	7.8	2.72	217.1	16.8	27.13	410	310	280	Clay
14	Fajar 1	7.6	8.32	177.1	3.5	30.1	370	500	130	Clay loam
15	Qal'a 1	7.2	9.18	150.0	3.7	16.1	200	510	290	Clay loam
16	Qal'a 2	7.0	8.18	207.5	2.0	23.2	250	360	390	Silty clay loam
17	Qal'a 3	7.2	9.21	152.5	3.4	19.2	160	480	360	Clay loam
18	Nasr 2	7.0	9.38	165.3	1.20	19.8	262	458	280	Clay loam
19	Nasr 3	7.1	10.20	147.5	1.9	20.2	300	400	300	Sandy Silt loam
20	Rifai 1	7.5	9.13	133.8	2.2	18.8	345	455	200	Silty clay loam
21	Rifai 2	7.5	13.22	144.0	2.9	19.4	200	400	400	Clay loam
LSD	0.899	2.665	2.532	0.889	0.889	4.447	4.447	4.447	0.899	

$$ESP = K_G.SAR \quad (4)$$

$$ESP = \frac{Na_x}{CEC} \times 100 \quad (5)$$

$$SAR = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}} \quad (6)$$

and magnesium). Gapon constant was calculated according to the equation of the US salinity laboratory.

ESP : Exchangeable Sodium Percentage

KG : Gapon constant

SAR : Sodium Adsorption Percentage.

RESULT AND DISCUSSION

Description of sodium status in studied soils

Dissolved Sodium in non-saline soils

Table 3 indicates that dissolved sodium values in non-saline soils ranged from 0.03-0.07 $mmol.L^{-1}$. This clearly reflects the chemical and physical properties of these soils on the dissolved sodium content in the soil. The dissolved sodium ranges in the solutions of these soils are wide. The ratio of sodium to calcium and magnesium ranged between (0.01-0.02) and (0.003-0.015), respectively. The ratio of sodium to the sum of

Table 3. Description of sodium status in the non-saline soil

Sample number	Locations	Dissolved ions ($mmol.L^{-1}$)				$\frac{Na}{Ca}$	$\frac{Na}{Ca}$	$\frac{Na}{\sum K+Ca+Mg+Na}$
		Na	K	Ca	Mg			
1	Fajar 3	0.04	0.06	3.0	6.0	0.01	0.006	0.004
2	Nasr 1	0.04	0.04	3.0	5.0	0.01	0.008	0.004
3	Rifai 3	0.07	0.04	4.0	7.0	0.02	0.01	0.006
4	Shatrah 1	0.03	0.04	2.0	2.0	0.015	0.015	0.007
5	Shatrah 2	0.04	0.05	4.0	3.0	0.01	0.01	0.005
6	Shatrah 3	0.03	0.09	2.0	3.0	0.015	0.01	0.005
7	Suq Al-Shuyukh 1	0.03	0.04	3.3	8.0	0.01	0.003	0.002
8	Suq Al-Shuyukh 2	0.04	0.07	5.0	4.0	0.01	0.01	0.004
9	Suq Al-Shuyukh 3	0.07	0.08	3.0	4.0	0.02	0.01	0.009
10	Nasiriyah 1	0.04	0.07	4.0	4.0	0.01	0.01	0.004
11	Nasiriyah 2	0.07	0.04	3.0	5.0	0.02	0.014	0.008
12	Nasiriyah 3	0.03	0.06	3.0	4.0	0.01	0.007	0.004

Table 4. Description of sodium status in the saline soil

Sample number	Locations	Dissolved ions (mmol.L^{-1})				$\frac{Na}{Ca}$	$\frac{Na}{Ca}$	$\frac{Na}{\sum K + Ca + Mg + Na}$
		Na	K	Ca	Mg			
13	Fajar 3	141	1.5	29	33	4.86	4.27	0.68
14	Fajar 1	277.8	2.3	34	52	6.7	5.34	0.75
15	Qal'a 1	179.2	2.4	171	223	1.04	0.80	0.31
16	Qal'a 2	572.6	2.2	137	193	4.17	2.96	0.63
17	Qal'a 3	755	2.2	26	736	29.03	1.02	0.49
18	Nasr 2	257.2	1.8	38	86	6.76	2.99	0.67
19	Nasr 3	258.2	1.7	39	85	6.62	3.03	0.67
20	Rifai 1	248.2	1.7	39	84	6.36	2.95	0.66
21	Rifai 2	248.2	1.7	38	84	6.53	2.95	0.67

positive and negative ions ranged between 0.002-0.009.

Status of dissolved Sodium in saline soils

Table 4 indicates that dissolved sodium values ranged between 141-755 mmol.L^{-1}, with an average of 326.38 mmol.L^{-1}, where the dissolved sodium content ranges in these soils are very wide, the percentage of sodium to both calcium and magnesium ranged between 1.04-29.03, with an average of 8.01 and 0.80-5.34, with an average of 2.92, respectively, that the sodium forms a very high proportion of calcium. In the same direction, the dissolved sodium in relation to the sum of positive and negative ions in the soil solution formed a percentage ranging between 31-75% and 61%. Fajar 1 recorded the lowest percentage of sodium relative to the total positive and negative ions while Al-Qal'a 3 location recorded the highest percentage, which reflects the characteristics of soils affected by salts on their content of dissolved sodium and this was confirmed by the subsequent statistical relations. When comparing the results (Al-fulahi, 2000), during the survey of sodium levels of the soil affected by salts in central and southern Iraq which obtained from locations in Al-Diwaniyah and Dujaila, which were used in the washing experiment, it was found that the percentage of sodium to both calcium and magnesium, the total positive and negative ions were 14.75, 5.2, 0.49, 0.15, respectively, which is lower

Table 5. Sodium adsorption Ratio SAR and exchange sodium percentage of non-saline soil

Sample number	Locations	SAR*10^3 Mmole.L$^{-1/2}$	ESP*10^3 Mmole.L$^{-1/2}$	K_G mol.L$^{-1/2}$
1	Fajar 3	18	3.6	20
2	Nasr 1	28	2.8	10
3	Rifai 3	16	4.5	28
4	Shatrah 1	21	3.4	16
5	Shatrah 2	17	3.3	19
6	Shatrah 3	12	3.9	32
7	Suq Al-Shuyukh 1	18	2.5	13
8	Suq Al-Shuyukh 2	21	2.4	11
9	Suq Al-Shuyukh 3	37	4.9	13
10	Nasiriyah 1	23	4.9	21
11	Nasiriyah 2	35	2.8	8
12	Nasiriyah 3	20	3.3	16
LSD		0.016	0.001	0.001

Table 6. Sodium Adsorption Ratio (SAR), Exchange Sodium Percentage (ESP) and Gapon constant KG in the saline soil

Sample number	Locations	SAR*103 Mmole.$L^{-1/2}$	ESP*103 Mmole.$L^{-1/2\ -1}$	KG*10^{-3} mol.$L^{-1/2}$
13	Fajar 3	25	332	13
14	Fajar 1	42	621	14
15	Qal'a 1	12	431	35
16	Qal'a 2	44	520	11
17	Qal'a 3	38	505	13
18	Nasr 2	32	495	15
19	Nasr 3	34	532	15
20	Rifai 1	31	515	16
21	Rifai 2	31	497	16
LSD		0.016	2.685	0.0039

than the percentages obtained in this study, especially in relation to the percentage of sodium to the sum of positive and negative ions.

Sodium Adsorption Ratio (SAR)

This ratio expresses the sodium ion density in the liquid soil phase according to the ratio law of SP. Scofield (1940), to the square root of calcium and magnesium. Table 5 shows that the variation characteristics of the chemical and physical soils have a significant effect on the variation in the values of the sodium adsorption ratios. The highest SAR value was recorded at Suq Al-Shuyukh-3 (37) non-saline soils while the lowest value was recorded was 12 at Shatrah-3 non-saline soils ,with an average of 22.2 mmol.$L^{-1/2}$.The results shown in Table 5 shows that the least significant difference was 0.016. In soils affected with salt, the highest SAR value was recorded in Al-Qal'a 2 area (44 mmol.$L^{-1/2}$) and the lowest value is 12 mmol.$L^{-1/2}$ at the Al-Qal'a-1 location. The high values of SAR values in soils affected with salt at Al-Qal'a location clearly reflect the effect of irrigation operations on quantity and quality on the values of sodium ratio in the saline solution, as well as the soil of the area cultivated or not cultivated as shown in Table 6.

Exchange sodium percentages (ESP)

The values of the exchange sodium percentage reflect the ability of the solid phase to adsorption of sodium due to various irrigation processes in quantity and quality. Table 6 indicates the values of the exchange sodium percentages for non-saline soils. The variation

Table 7. Some thermodynamic parameters for assessing sodium status in the non-saline soil

Locations	The ionic strength (mol×10^{-3}.L^{-1})	Sodium effectiveness factor f_{Na}	Sodium effectiveness a_{Na} (mol×10^{-3}.L^{-1})	Sodium potential P_{Na}-Log a_{Na}	pH
Fajar 3	74.30	21.83	873.2	2.94	7.8
Nasr 1	26.65	7.6	532	2.73	7.8
Rifai 3	84.11	24.77	743	2.87	7.6
Shatrah 1	24.7	6.98	209	2.32	7.9
Shatrah 2	3.38	0.68	20	1.30	8.2
Shatrah 3	0.39	0.07	2.1	0.32	7.8
Suq Al-Shuyukh 1	0.91	0.02	0.8	0.10	7.6
Suq Al-Shuyukh 2	1.69	0.227	8.8	0.94	7.8
Suq Al-Shuyukh 3	0.26	0.09	6.3	0.79	7.8
Nasiriyah 1	3.961	0.83	33	1.52	7.7
Nasiriyah 2	1.04	0.05	3.5	0.54	7.9
Nasiriyah 3	0.91	0.03	1.2	0.08	7.8

Table 8. Some thermodynamic parameters for assessing sodium status in the saline soil

Locations	The ionic strength ($mol \times 10^{-3}.L^{-1}$)	Sodium effectiveness factor f_{Na}	Sodium effectiveness a_{Na} ($mol \times 10^{-3}.L^{-1}$)	Sodium potential P_{Na}-Log a_{Na}	pH
Fajar 3	108	31.9	449	2.65	7.6
Fajar 1	119	35.2	978	2.99	7.2
Qal'a 1	106	31.3	561	2.75	7.0
Qal'a 2	119	35.2	202	2.31	7.2
Qal'a 3	121	35	264	2.42	7.0
Nasr 2	132	39	100	2	7.1
Nasr 3	118	34	878	2.9	7.5
Rifai 1	171	50.8	126	2.1	7.5
Rifai 2	204	60.1	149	2.2	7.4

in the values of the Exchange Sodium Percentages (ESP) of non-saline soils soil clearly reflects the variation of soils in terms of texture, type of clay minerals, organic matter and competing ions, while continuous irrigation and poor water use at Nasiriyah led to a significant increase in the values of exchange of sodium percentages. As it amounted at non-saline soils location which was taken for comparison (0.049) and increased as a resulting of salinization due to excessive irrigation and non-use of leaching requirements. The values obtained are consistent with Kourgialas (2016). This may be due to saline conditions that increase the preference for adsorption of low-charge positive ions such as sodium with increasing saline concentration of the soil solution. In contrast, the leaching process led to increase the preference for binary ions such as calcium and magnesium according to the concept of valence dilution effect (Bohn *et al*., 2001).

Gapon constant KG

Gapon constant reflects a characteristic trait of the soil and the extent to which the soil is preferred to the different ions during the substitution interactions between the solid and liquid soil phases. Cation selectivity coefficient is the most important criterion when studying the surface chemistry of the soil. Table 7 indicates that the sediments had a preference coefficient ranging from 0.008 in Nasiriyah location to 0.032 $mol.L^{-1/2}$ in Al-Shatrah location. The lowest significant difference was 0.001. The salinization processes at Nasiriyah location led to a decrease in the values of the Gapon constant KG from 0.008-0.032 $mol.L^{-1/2}$. The low values reflect the low capacity of sodium adsorption, unlike high-value soils expressing a high tendency for adsorption of sodium. The decrease in the values of Gapon constant KG is due to the effect of the release of calcium and magnesium ions to the solution due to the increase in salinity. This results in higher values of sodium adsorption ratio is relative to increasing the preference of the calcium ion exchange complex. These results agree with Frenkel and Alper (1984).

At low levels of salinity, as in non-saline soils, the solubility of calcium carbonate, primary calcium-bearing minerals will reduce the values of sodium adsorption ratio of the liquid soil phase, resulting in higher capon constant values. The values obtained are consistent with Kourgialas (2016), which indicated that the average of Gapon constant for four soil affected with salts from different locations of Al Qal'a was 0.035 $mol.L^{-1/2}$. The results obtained by the salinity laboratory were in accordance with the Soil Survey Staff (1951), Al-Zubaidi and Hardan (1972). The Gapon constant values were 0.01457, 0.015 $mol.L^{-1/2}$ respectively. In the soils affected with salts it was clear that the values of Gapon constant were significantly affected with the Sodium Adsorption Ratios (SAR). The values of the Gapon constant were also affected by ESR values, which confirms the high correlation between ESR and SAR. and the solution of its equilibrium in determining

Gapon constant. This agrees with *et al*. (1975). that increased soil interaction which will lead to increase ion exchange capacity and surface charge density which increases ionic preference for sodium.

Thermodynamic parameters of dissolved sodium in soil

Effectiveness factor of sodium

Table 7 indicates that the sodium effectiveness coefficient is between (0.02 and 24.77). Therefore, about 9% of sodium solution of the non-saline soils is ineffective which recorded the lowest value of the ionic effectiveness coefficient at Suq Al-Shuyukh 1 location and the highest value recorded in Rifai 3. In saline soils, Table 7, the ionic effectiveness coefficient of sodium ranged from 31.2 to 60.1, where 57% of sodium is ineffective in saline soils, on the whole more than in non-saline soils soils by (6 times) which clearly reflects the effect of ionic ion efficiency on the ionic strength of the soil solution.

Sodium effectiveness

The difference in the chemical and physical properties of the soil, especially the liquid soils phase and their ionic strength, had an effect on the sodium effectiveness values. The lowest ionic effectiveness were recoded (10-3 × 8 mol.$L^{-1/2}$) in Suq Al-Shuyukh1 while the highest ionic effectiveness was 10-3 × 873 in Fajar-3 location as shown in Table 7. As for saline soils, the values of sodium effectiveness varied according to the different soils. The lowest value was recorded (100 mol.$L^{-1/2}$) at Nasr 2 and the highest value was recorded (978 mol.$L^{-1/2}$) at Fajar-2 location, the non-saline soils were characterized by ionic effectiveness less than the ionic effectiveness of sodium in saline soils as shown in Table 8. This can be attributed to the role of ionic strength of non-saline soils in reducing sodium effectiveness factor on the one hand and to possible formation of ionic dual for sodium, especially with sulphate, thus reducing the effectiveness of the liquid phase of non-saline soil.

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