KINITEC DESCRIPTION OF SODIUM BEHAVIOR IN SOME AFFECTED AND NON-AFFECTED SOILS BY SALTS

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ABSTRACT

This study included different soil locations around Mosul city representing non salt affected soils, and around Basrah city representing salt – affected soil. The aim of this study is to show the behavior of sodium due to first order and diffusion equations, using miscible displacement at different times (10, 20, 30, 60, 90, 120, 180, 360, 480, 600, 720 minute). The results indicate that the solubility and release of sodium decreases with time, but according to kinetic concept the cumulative of sodium solubility increased in the two type of soils study. However, salt affected soils showed more solubility and release of sodium than the non-salt affected soils. While the diffusion equation gave the best description of sodium solubility depending on the coefficient determination and standard error. Selectivity coefficient of Gapon due to the chemical concept K_G, thermodynamic concept K_G^- and sposito concept $K_G^=$ were also examend which showed that the values K_G , K_G^- decreased with time , while $K_G^=$ values increased over time.

Key words : Gapon equation , SAR , adj SAR , kinetic , thermodynamic.

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INTRODUCTION

Selectivity coefficient of Gapon (K_G) represents the tendency of linear relationship between SAR(sodium adsorption ratio) – ESR (exchangeable sodium ratio) when applied on affected soils and non- affected soils by salts, this coefficient was used to control the behavior of sodium through the two parameters as mentioned above, which influenced by some soil properties including concentration of electrolytes, clay minerals, organic colloids, sodium in both solid and liquid phase of soil (Jurinak et al., 1984 and Amrhien and Suarez ,1991). So the study of ion selectivity descripe the interaction between positive ion and surface exchange and water. It is also considered as an approach to understanding the movement of soluble components within the soil which represent surface chemistry of soils (Thomas, 1977). The Gapon equation is one of the most applied equation, especially in salt affected soils it was then developed by USA salinity Laboratory by inserting magnesium into both end of the equation and the regression value of linear relationship between SAR-ESR express the selectivity coefficient of Gapon (Paliwal and Gandhi, 1976) and (Farahmand et al., 2009). Thus, recent studies have used the kinetic concept in the description of many interaction that occur between the liquid phase and the exchange surface through using kinetics equation, but the preference between them depends statistically on the determination coefficient R^2 and standard error SE (Ogwada and Sparks, 1986). There are many techniques used to study kinetic approach of sodium such as miscible displacement (Sparks et al., 1980 b). There are some disadvantage in Gapon equation when was using to descripe the exchange between Na^{+} - Ca^{++} on the solid phase of soil, according to (Sposito, 1977) the concept of mole fraction were used to calculate the activity of exchange surface.

MATERIALS AND METHODS

Various locations were choosen around Mosul city (Gogjali , Taharawa , Bartella , Karamlease , Al-Abbasiah , Khursibat , Filfeal , Badoosh , Salamiah , Hamdaniah) represent soils non-affected by salts, and another locations around Basrah (Hamdan , Al-Fao , Abu-Alkaseeb) represent soils affected by salts. Soil samples were drying and sieved by 2 mm sieves in order to be ready for laboratory analysis. Some physical and chemical properties were estimated as shown in table (1 and 2) according to the methods given in (Carter and Gregorich , 2008 and Rowell , 1996 and Tandon, 1999). So miscible displacement was used to study the Kinetic approach of sodium, and sodium ion was selective using plastic columns with dimentions (15 cm L , 4 cm diameter) , 20gm of soil was putted in each column, soil lifted to balance with distilled water for 24 hours, different time were used as follows 10 , 20 , 30 , 60 , 90 , 120 , 180 , 240 , 360 , 480 , 600 , 720 minute . The extract was then collected from the soil column at each time to estimate. Both calcium and magnesium were determination by titration with versenate solution 0.01 M, and sodium by flame photometer according to Sparks et al., 1980 b . So the diffusion equation was to descripe the solubility of sodium using mathematical formula as follows:

$$C_t = C_o + K\, t^{1/2}$$

C_t: conc.of sodium at limited time.
C_o: conc.of sodium at zero time.
$t^{1/2}$: time
K: rate coefficient of sodium solubility.

Table (1): Some physical and chemical properties of study soils

locations	pH	EC ds.m^{-1}	organic matter gm.kg^{-1}	$CaCO_3$ gm.Kg^{-1}	Soil particles gm.Kg^{-1}			
					clay	silt	sand	texture
Gogjali	7.57	0.21	11.68	188.2	342	372	286	Clay loam
Taharawa	7.57	0.22	18.91	193.1	291	403	306	Clay loam
Bartella	7.66	0.21	7.20	194.6	441	322	237	Clay
Karamlease	7.62	0.25	28.53	220.3	391	323	286	Loam clay
Abbasiah	7.65	0.16	17.87	256.5	242	422	336	Loam
Khursibat	7.55	0.23	21.30	270.8	392	422	186	Silty clay loam
Filfeal	7.57	0.19	22.34	168.2	366	297	337	Clay loam
Badoosh	7.62	0.18	10.30	294.2	366	448	186	Silty clay loam
Sallamiah	7.56	0.37	61.21	140.3	372	352	276	Clay loam
Hamdaniah	7.62	0.20	24.41	231.6	316	398	286	Clay loam
Hamdan	7.60	1.64	20.39	62.6	341	422	237	Clay loam
Al-fao	7.00	13.76	25.89	109.0	391	323	286	Clay loam
Al-Seebah	7.20	3.77	22.70	210.9	241	473	286	Loamy
Abu- Al-Khaseeb	7.34	5.98	31.00	137.3	391	273	336	Clay loam

Table (2): soluble cations and anions in the studies soils

Locations	Cations mmol.l^{-1}				Anions mmol.l^{-1}		
	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^-	Cl^-	$SO_4^=$
Gogjali	1.50	1.42	0.31	0.21	4.40	1.53	1.83
Taharawa	2.31	1.50	0.31	0.30	4.85	2.17	1.64
Bartella	1.53	2.11	0.17	0.23	3.50	1.46	1.42
Karamlase	1.75	1.33	0.17	0.46	4.12	1.58	2.80
Abbasiah	1.91	1.20	0.13	.0 15	3.75	1.50	1.85
Khursibat	1.62	1.45	0.37	0.17	4.15	2.55	2.40
Filfeal	1.67	1.37	0.17	0.12	3.85	2.13	2.48
Badoosh	1.82	0.97	0.21	0.22	3.20	2.20	2.63
Sallamiah	1.90	1.82	0.17	0.71	4.35	22.34	2.99
Hamdaniah	1.55	1.46	0.19	0.41	4.27	1.72	1.99
Hamdan	2.21	1.81	13.47	0.25	5.73	10.31	0.36
Al-Fao	12.33	4.73	52.17	1.69	3.70	20.64	1.72
Al-Seebah	10.64	6.25	37.82	2.71	4.25	9.12	1.25
Abu- Al-Khaseeb	11.26	5.19	27.39	3.10	4.12	9.56	0.94

RESULTS AND DISCUSSION

Kinetic K_G according chemical thermodynamic and sposito concept:

The theoretical approach of kinetic concept is based on the rate of reaction, which is in a state of proportion with the concentration of reactant substances and the substances resulting from the reaction, this rate represents the differentiation concentration of matter with time $r = \frac{dc}{dt}$ Therefore , the study of kinetics aims to obtain a sufficient information about the behavior and rate of reaction which is added to the knowledge of the change in concentration of reactant and resultant substances over time as well as the effect of temperature on the rate and mechanism of reaction (Goyal and Rani , 2011 and Sparks , 1989). Results showed from the table (3) that the selectivity coefficient of Gapon in salt affected soils which affected by the concentration of sodium in soil solution, rate of solubility, desorption, temperature. The table (3) shows that the values of Gapon selectivity coefficient according to the chemical concept were low in the first time indicated by value (0.16 , 0.16 , 0.17 $L.mol^{-1}$) at times (10 , 20 , 30 minute) for Karamlease soil. This behavior affected by sodium adsorption ratio in the equilibrium solution, whose values were high because the K_G values were decrease, but these values increase over time which reached to (48.83).

Table (3): Kinetic approach of Gapon constant due to chemical, thermodynamic, sposito concept in some soil non-affected by salts

Time minute	Karamlease $L.mol^{-1}$			Khursibat $L.mol^{-1}$			Badoosh $L.mol^{-1}$		
	K_G	K_G^-	$K_G^=$	K_G	K_G^-	$K_G^=$	K_G	K_G^-	$K_G^=$
10	0.16	0.11	0.58	0.04	0.03	0.93	0.07	0.19	0.63
20	0.16	0.11	0.58	0.06	0.04	0.84	0.11	0.28	0.52
30	0.17	0.11	0.55	0.08	0.06	0.81	0.13	0.31	0.45
60	0.18	0.12	0.53	0.08	0.06	0.77	0.14	0.34	0.44
90	0.19	0.12	0.47	0.09	0.06	0.72	0.14	0.34	0.44
120	0.19	0.13	0.46	0.11	0.07	0.67	0.15	0.35	0.42
180	0.23	0.13	0.46	0.11	0.08	0.66	0.15	0.36	0.42
240	0.20	0.13	0.43	0.13	0.07	0.59	0.17	0.34	0.42
360	0.24	0.16	0.42	0.16	0.07	0.52	0.16	0.36	0.38
480	0.27	0.17	0.42	0.17	0.08	0.37	0.17	0.34	0.39
600	0.31	0.18	0.40	0.17	0.09	0.41	0.19	0.33	0.37
720	0.33	0.21	0.41	0.16	0.09	0.40	0.19	0.30	0.34

at the last time of experiment. The low values of K_G indicated that these soils having low capacity to adsorped sodium against to salt affected soils, The higher values reflect the tendency of K_G values were decrease, but these values increase over time which reached to (48.84) at the last time of experiment. The low values of K_G indicated that these soils having low capacity to adsorped sodium against to salt affected soils, The higher values reflect the tendency of soils to adsorb sodium (Abdul-Ghafoor et al. , 2004). As for the Gapon constant K_G according to thermodynamic concept, it is clear that the three soils (Karamleas , Khorsibat , Badoosh) with K_G values are low (0.11 , 0.03 , 0.19) in the soils above respectively. But these values increase with the end of time to reach (0.21 , 0.09 , 0.30) as a result of SAR from low values to high values up to the last time. When we are consider the Gapon constant according to the concept of Sposito the table (3). show that the K_G in the three soils behaved reversible, meaning that the $K_G^{=}$ values were high in the first time (0.58 , 0.93 , 0.63) in the three soils respectively then the $K_G^{=}$ were reduced as time progresses to reach (0.41 , 0.40 , 0.34). These high values of $K_G^{=}$ indicate clearly, exchange sodium ratio (ESR) of the solid phase exceeds the SAR in the liquid phase in the first time, and then this state was reversibly to decrease the $K_G^{=}$ values with increasing in the selectivity for these soils to calcium and magnesium against sodium (Farahmand et al. , 2009). Soils affected salts (Al-Fao ,Al-Seebah , Abu-Alkhaseeb) were show a difference in the values of K_G , K_G^{-} , $K_G^{=}$ (table 4). Where's K_G and K_G^{-} values reached to (48.83 , 37.80) and (12.44 , 26.72) and (9.33 , 19.40) in the three soils respectively. According to chemical and thermodynamic concept When tracking the behavior of K_G values in these soils, we find that there is a difference in K_G values of K_G , K_G^{-} , $K_G^{=}$. The values of K_G and K_G^{-} increase in the three soils with increasing time of experiment, however in the three soils, the values of K_G and K_G^{-} in Al-Fao soil according to chemical and thermodynamic concept are superior to the soil of Al-Seebah and Abu-Alkhaseeb as indicated by high values (48.83 , 29.36 , 32.83) soils respectively. The superiority of ESR values on SAR in these times and K_G begin to decrease with time to reach (0.35 , 0.67 , 0.50) in the three soils at the last time 720 minutes respectively.

Kinetics approach of sodium:

The Kinetics of chemical reactions considered one of the concept of physical chemistry because they deal with the rate of interactions which depend on the concentrations of substances involved in the reaction. The rate of reaction is expressed by the rate of change in the concentration of reactants or resultants for time, this is why chemical reaction occur in different stage (Sparks , 1989). In order to apply this approach on the study soils to determine the rate coefficient of sodium solubility using Kinetic equations. The table (5) shows that the coefficient solubility rate of sodium according to the slope of first order and diffusion equations have differed and varied between increasing and decreasing within the soils, affected or non-affected by salts. The highest rate solubility (1.14 $min.^{-1}$) was recorded in the Al-Abbasiah soil, while the lowest value of this coefficient (0.04 $min.^{-1}$) was recorded in Gogjali soil. The diffusion equation gave a higher values of rate solubility relatively to the first order equation, reached to the higher value in

Taharawa soil (0.27) and the lowest value in Sallamiah soil (0.07). These equations are also applied on the salt affected soils as shows (table 5), that the values of sodium solubility in the first order equation were fairly similar with the soils non-affected by salts ranging (0.07 – 0.96).
While the values of rate solubility when apply the diffusion equation were higher in salt affected soils compared to the values in soils non-affected by salts ranged from (3.46 – 18.28) which indicated that the sodium was sourced from dissolved salts, but the sodium which has dissolved or leached from soils non-affected by salts is due to the solubility of minerals bearing this element (Sparks, 1999 and Goyal and Rani , 2011).

Table (4): Kinetic approach of Gapon constant due to chemical, thermodynamic , sposito concept in soils affected by salts

Time minute	Al-Fao $L.mol^{-1}$			Al-Seebah $L.mol^{-1}$			Abu- Al-Khaseeb $L.mol^{-1}$		
	K_G	K_G^-	$K_G^=$	K_G	K_G^-	$K_G^=$	K_G	K_G^-	$K_G^=$
10	0.03	0.01	37.04	0.03	0.01	29.36	0.04	0.02	32.83
20	0.05	0.03	29.95	0.05	0.02	19.86	0.04	0.02	31.48
30	0.12	0.08	18.25	0.12	0.07	11.37	0.06	0.04	24.80
60	1.03	0.22	12.64	0.35	0.13	7.20	0.13	0.07	15.33
90	1.55	0.51	9.94	1.47	0.26	2.80	2.51	0.23	9.23
120	2.68	0.86	5.25	1.67	1.31	1.71	2.35	1.15	4.63
180	7.15	1.55	4.03	1.87	1.57	0.82	2.50	1.07	1.98
240	19.79	4.22	2.12	1.88	3.31	0.74	3.43	1.15	1.31
360	27.61	16.41	0.94	2.83	9.14	0.74	3.75	4.53	0.77
480	39.43	27.85	0.52	6.71	17.52	0.67	5.61	8.62	0.63
600	41.24	35.50	0.47	10.61	19.33	0.68	7.26	13.57	0.50
720	48.83	37.80	0.35	12.44	26.72	0.67	9.33	19.40	0.50

Mathematical description of sodium kinetic solubility:
The coefficient limitation (R^2) and standard error (SE) were used to evaluate and descripe the kinetic equations in order to descripe the best equation of sodium behavior of sodium in these soils.

Table (5): Rate coefficient of sodium solubility by using first order and diffusion equation

Non-affected soils				
Locations	First order		Diffusion	
	slope	Linear regression	slope	Linear regression
Gogjali	0.04	Y= 0.0004 X + 0.2276	0.31	Y= 0.3102 X + 2.2346
Taharawa	0.12	Y= 0.0012 X + 0.2003	0.27	Y= 0.2797 X + 0.4395
Bartella	0.05	Y= 0.0005 X + 1.9492	0.10	Y= 0.1055 X + 0.2541
Karamlease	0.05	Y= 0.0005 X + 1.155	0.14	Y= 0.1434 X + 0.1612
Abbasiah	1.14	Y= 0.0114 X + 1.9154	0.08	Y= 0.0864 X + 0.0377
Khursibat	0.90	Y= 0.009 X + 0.6967	0.14	Y= 0.1402 X + 0.5921
Filfeal	0.95	Y= 0.0095 X + 0.4433	0.18	Y= 0.1829 X + 06257
Badoosh	0.30	Y= 0.003 X + 1.2833	0.10	Y= 0.1086 X + 0.2379
Sallamiah	0.05	Y= 0.0005 X + 1.8483	0.07	Y= 0.0742 X + 0.0268
Hamdaniah	0.23	Y= 0.0023 X + 1.3494	0.09	Y= 0.0997 X + 0.0361
affected soils				
Locations	First order		Diffusion	
	slope	Linear regression	slope	Linear regression
Hamdan	0.01	Y= 0.0177 X - 3.1364	3.47	Y= 3.4723 X + 23.46
Al-Fao	0.04	Y= 0.0459 X - 6.7524	13.09	Y= 13.09 X + 1288.2
Al-Seebah	0.18	Y= 0.188 X - 8.3067	3.46	Y= 3.4665 X + 578.05
Abu- Al-Khaseeb	0.96	Y= 0.965 X – 7.72	18.28	Y= 18.285 X + 1050.9

Table (6): Regression analysis of the best kinetic equation used to descripe sodium solubility

Non-affected soils				
Locations	First order		Diffusion	
	R^2	SE	R^2	SE
Gogjali	0.97	4.22	0.81	3.00
Taharawa	0.94	3.87	0.95	0.93
Bartella	0.97	1.11	0.85	0.99
Karamlease	0.89	1.27	0.97	0.42
Abbasiah	0.85	4.51	0.98	0.14
Khursibat	0.98	1.50	0.96	0.28
Filfeal	0.98	1.48	0.94	0.69
Badoosh	0.96	0.49	0.98	2.99
Sallamiah	0.74	1.04	0.96	0.15
Hamdaniah	0.89	0.73	0.97	0.22
affected soils				
Locations	First order		Diffusion	
	R^2	SE	R^2	SE
Hamdan	0.90	8.40	0.95	7.94
Al-Fao	0.93	6.13	0.87	5.24
Al-Seebah	0.90	7.92	0.98	6.60
Abu- Al-Khaseeb	0.90	9.12	0.96	5.12

The results (Table 6) showed that the values of R^2 in the non-affected soils by salts ranged from (0.74 – 0.98) and SE between (0.49 – 4.51) in the first order equation, while the values of R^2 in the diffusion equation between (0.85 – 0.98) and SE between (0.14 – 3.00). Referring to soils affected by salt it was observed that the values of R^2 were between (0.90 – 0.93) and SE between (6.13 – 9.12) in the case of the first order equation, but the values of R^2 at diffusion equation are (0.87 – 0.98) with standard error (5.12 – 7.94). Results indicated that the diffusion equation gave the best description for sodium solubility because it take the highest coefficient determination R^2 and least standard error compared to the first order equation in all soil affected and non-affected by salts, these results were agreement with previous studies that used kinetic approach (diffusion equation) to descripe the sodium solubility especially in salt affected soils because the reaction controlled by two ways, rate of reaction and pathway of reaction that happen to salts containing sodium (Buentt, 1986 and Sparks , 1989).

حركيات وصف سلوك الصوديوم في بعض الترب المتأثرة وغير المتأثرة بالاملاح

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الخلاصة

شملت الدراسة مواقع لترب مختلفة حول مدينة الموصل تمثل الترب غير المتأثرة بالأملاح ومواقع حول مدينة البصرة تمثل الترب المتأثرة بالأملاح بهدف دراسة السلوك الحركي للصوديوم اعتمادا على معادلة الرتبة الاولى ومعادلة الانتشار باستخدام طريقة الازاحة الامتزاجية في أزمنة مختلفة (10 ، 20 ، 30 ، 60 ، 90 ، 120 ، 180 ، 240 ، 360 ، 480 ، 600 ، 720 دقيقة). أشارت النتائج الى ان ذوبان وتحرر الصوديوم يقل مع الزمن ولكن حسب المفهوم الحركي يزداد تجميعيا في نوعي الترب المستخدمة في الدراسة. إلا أن الترب المتأثرة بالأملاح أظهرت ذوبان وتحرر أكثر للصوديوم مقارنة بالترب غير المتأثرة بالأملاح حيث أعطت معادلة الانتشار أفضل وصف لذوبان وتحرر الصوديوم اعتمادا على معامل التحديد R2 والخطأ القياسي SE كما تضمن البحث دراسة معامل التفضيل لگابون حسب المفهوم الكيميائي KG والمفهوم الثرموديناميكي -KG ومفهوم KG= Sposito فقد أوضحت النتائج أن قيم KG و -KG تقل مع الزمن في حين تزداد قيم =KG مع مرور الزمن.

الكلمات المفتاحية : معادلة كابون, SAR, Adj ASR, حركيات, ثرموداياناميك

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