PAPER • OPEN ACCESS

Study of Na & Ca Exchange Relations and Selectivity Coefficient of Drained Marsh Soils in Southern Iraq

To cite this article: B H Jabr *et al* 2023 *IOP Conf. Ser.: Earth Environ. Sci.* **1252** 012055

Study of Na & Ca Exchange Relations and Selectivity Coefficient of Drained Marsh Soils in Southern Iraq

B H Jabr, M M Yassin, and S M Sultan
Department of Soil and Water Resources, College of Agriculture, University of Basra, Basrah, Iraq
Corresponding Author's E-mail: baidaa.jaber@uobasrah.edu.iq

Abstract: This study was carried out in some soils of dried marshes in the governorates of Basra, Dhi Qar, and Maysan in southern Iraq. The sites for six pedons were selected Shafi-Al, Al-Mashab, Al-Chibayish, Al-Hammar, Al-Azim، and Al-Musharrah. Their coordinates were determined using a GPS device. Through the quantitative calculation of the selectivity coefficient in the ion exchange system according to Gapon (KG)and Vanselow (KV) at the ratios (2:8) and (8:2) sodium-calcium and for concentrations of 100,200, 400, and 800mmol$_c$liter^{-1}, their coordinates were determined in order to determine the reciprocal relationship between calcium and sodium as well as the extent of selectivity of the study soils for any of the two ions. The results showed that all the soils under study tended towards a preference for calcium by binding at the exchange sites compared to the sodium ion, and it showed a high preference for the study soils for calcium compared to sodium in low salt concentrations preference decreased with increasing salinity. The results of the study for the linear relationship between each of the values of the coefficient of preference (KG and KV) and the clay separation at the different soils of the study showed that there is a highly significant negative correlation (r) (-0.878 and - 0.9516) at the ratio 8:2 sodium: calcium, respectively. While no correlation appeared when studying the relationship between the selectivity coefficient constants (KG and KV) and each of the organic matter and the degree of soil reaction (pH) and lime (CaCO3).
Keywords: drained marsh soils, Cation exchange, selectivity coefficient, Gapon and Vanselow equation

1. Introduction

The marshes are a prominent feature of the southern alluvial plain of Iraq, which is bounded by the governorates of Suq al-Shuyukh in the west, Basra in the south and east, and Maysan in the north. The area of marshes covers around 20,000 square kilometers [1]. By losing 94% of the water in these water bodies during the past two decades, the marsh environment has experienced significant environmental change. Many significant soils characteristics, such as salt content expressed in electrical conductivity (ECe), soil reaction degree (pH), calcium carbonate (CaCO3), and cation exchange capacity will be clearly impacted by the unexpected change in environment from being submerged in water for extended periods to a dry environment (CEC). Along with some morphological changes, the process also affects the content of organic substances and other aspects of the environment. Moreover, the repeated drying and wetting cycles may have an impact on the soil's mineral characteristics and nutrient availability, notably on clay minerals, which are thought to be the active part of the soil colloidal due to their high specific surface area, Cation exchange capacity, are the effective mineral and colloidal components. These reciprocal properties play an effective role in many physicochemical and chemical reactions represented by the adsorption, exchange, and ionic releasing of nutrients. The aim of the study is to know the nature of the selectivity or optional ness of these soils for some of the ions present in the soil solution due to the considerable significance it bears in the reclamation, management, and exploitation of these soils.

2. Materials and Methods

2.1. Soil samples

Six pedons were selected representing three paths covering most of the marshes in southern Iraq, namely
1- The first track towards Basra covers:

- the Al-Shafi; N 30º 55' 01.2"; E 47º 24 47.7"
- Al-Mashab marshes: N 30º 36' 00.6"; E 47º 37' 57.2"

2- The second path towards Dhi Qar covers:

- the Chibayish: N 30º 57' 15.4" ; E 47º .00 26.9"
- Al-Hammar marshes: N 30º 56' 43.9" ; E 46º .50 26.8"

3 - The third path towards Maysan covers :

- the Al-Azim : N 30º 55' 31.5" ; E 46º .44' 35.9
- Al-Musharrah marshes : N 31º 46' 45.0" ; E 47º . 27'. 40. 0"

It shows (Fig. 1) the geographical locations of these marshes chosen for the study.

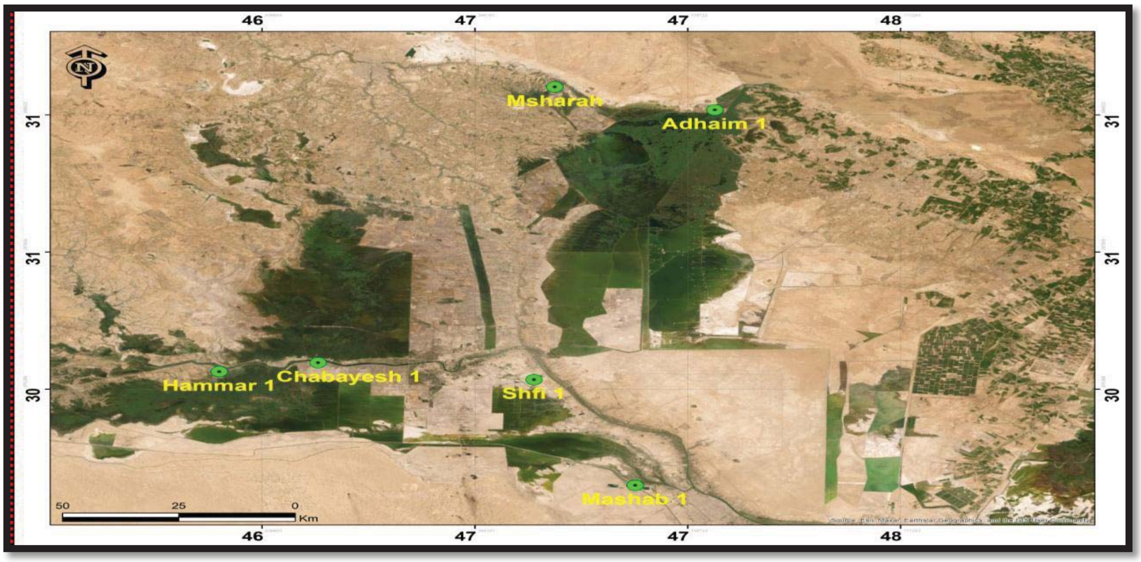

Figure 1. The image representing the Study Sites

After identifying the sites required for the study, excavating the soil section ،and describing its morphology, representative soil samples were taken for each horizon, the soil samples were air-dried, crumbled manually and with a wooden hammer, passed through a sieve with a diameter of (2 mm) and kept in plastic boxes. chemical and physical analyses were carried out according to the results shown in Tables 1 and 2 according to the methods adopted by [2].

Table 1. Particle-size distribution and soil texture of the horizons of pedons, Basra, Thi-Qar, and Maysan province

Pedons number	Location	horizon	depth (cm)	Particle-size distribution ($g\ Kg^{-1}$)			soil texture
				Sand	Silt	Clay	
P_1	Basra / Al-Shafi	A	0 - 28	49.50	545.82	404.68	SIC
		C_1	28 - 71	138.93	482.49	378.58	SICL
		C_2	+113	180.00	488.82	331.18	SICL
P_2	Basra/Al- Mashab	A	0 - 21	125.08	420.44	454.48	SIC
		C_1	+90	158.95	471.96	369.09	SIC
P_3	Thi-Qar/Al- Jabayish	A	0-20	211.69	356.75	431.56	C
		C_1	20 – 35	219.89	376.15	403.96	C
		C_2	35 – 81	185.00	405.00	410.00	SIC
		C_3	+116	171.30	409.7	419.00	SIC
P_4	Thi-Qar/ Alhimar	A	0 - 22	218.14	376.55	405.31	C
		C_1	22 - 46	167.75	404.01	428.24	SIC

IOP Conf. Series: Earth and Environmental Science 1252 (2023) 012055 doi:10.1088/1755-1315/1252/1/012055

		C_2	+ 99	165.50	387.50	447.00	**C**
P_5	Maysan / Aleazim	**A**	0 - 19	100.06	401.00	498.94	**SIC**
		C_1	+ 41	187.34	406.25	406.41	**SIC**
P_6	Maysan / Al-Musharrah	**A**	0 - 18	124.38	410.35	465.27	**SIC**
		C_1	18 - 57	126.86	385.27	487.87	**C**
		C_2	+100	120.67	386.34	492.99	**C**

Table 2. Some chemical properties of the horizons of pedons, Basra, Thi-Qar, and Maysan province

Pedons number	**Location**	**horizon**	**depth (cm)**	**pH**	**EC**	**Carbonate mineral**	**Organic matter**	**CEC cm mol$_c$ kg^{-1}**
					dS m^{-1}	**g kg^{-1}**		
P$_1$	**Basra / Al-Shafi**	**A**	0 - 28	7.48	62.80	346.66	9.26	21.94
		C$_1$	28 - 71	7.81	60.20	285.00	8.01	18.80
		C$_2$	113 +	7.64	54.20	266.67	5.25	12.67
P$_2$	**Basra/Al-Mashab**	**A**	0 - 21	7.76	25.00	375.00	17.36	23.46
		C$_1$	90 +	7.47	35.14	296.47	6.86	14.13
P$_3$	**Thi-Qar/Al- Jabayish**	**A**	0-20	7.51	12.42	255.00	38.75	33.20
		C$_1$	20 – 35	7.53	18.82	218.40	34.31	28.47
		C$_2$	35 – 81	7.49	27.00	298.23	2.72	16.40
		C$_3$	+116	7.50	14.24	305.00	1.88	15.93
P$_4$	**Thi-Qar/ Alhimar**	**A**	0 - 22	7.40	40.03	158.43	9.17	26.93
		C$_1$	22 - 46	7.54	50.40	146.56	2.48	24.34
		C$_2$	99+	7.66	40.80	145.00	1.75	17.87
P$_5$	**Maysan / Aleazim**	**A**	0 - 19	7.92	29.18	266.62	22.27	28.00
		C$_1$	41+	7.39	31.30	230.00	11.97	18.80
P$_6$	**Maysan / Al-Musharrah**	A	0 - 18	7.70	2.62	246.36	32.47	34.57
		C$_1$	18 - 57	7.50	7.83	255.00	18.19	27.60
		C$_2$	+100	7.48	13.36	246.36	7.37	19.60

2.2. Experimental Application

One gram of the study's sample soils was placed in centrifuge tubes, washed several times with distilled water, and treated with ten milliliters of an equilibrium solution that had been prepared at concentrations of 100, 200, 400, and 800 meq L-1 with ratios of (Ca: Na) (2:8 and 8:2) for each concentration. The mixture was then shaken vigorously for a quarter of an hour with an electric shaker.

this process was repeated Three times to guarantee that the exchange complex reached its saturation condition before separating the clear liquid from the sediment using a centrifuge. Three times of alcohol were used to remove the extra ions from the soil. The extracted exchanged ions were then purified with 1 magnesium nitrate, and the amount of sodium freed was calculated using a pyrophoresis equipment. Using calculations , the following equation was used to determine the calcium exchanged:

Ex Ca= CEC – Ex Na ……….(1)

Where Ex Ca and Ex Na represents excrepresentium and calcium, respectively.

The following ion exchange equations require you to calculate the selectivity coefficient of the ion exchange constant:

1) Gapon (1933): $KG = \frac{Ex_{Na}\,[Ca]^{0.5}}{Ex_{Ca}\,[Na]}$ …………(2)

2) Vanselow (1932):- $KV = \frac{M^2{}_{Na}\,(Ca)}{M_{Ca}\,(Na)^2}$. ……..(3)

Where, Ex Na represents the exchanged sodium $cmol_c\ kg^{-1}$

Ex Ca represents exchangeable calcium $cmol_c\ kg^{-1}$

M Na is the molar fraction of exchanged sodium

M Ca is the molar fraction of exchanged calcium

[Na] is the sodium concentration in the $m\text{-}eq^{-1}$ equilibrium solution

[Ca] represents the calcium concentration in the $m\text{-}eq^{-1}$ equilibrium solution

(Na) represents the sodium activity in the $meqL^{-1}$ equilibrium solution

(Ca) represents the calcium activity in the $meq\ L^{-1}$ equilibrium solution

CEC represents the exchange capacity of positive ions, centimole kg^{-1}

KG and KV represent the ion exchange constants according to Gapon and Vanselow in sequence.

In accordance with the activity (activity) of the ions in the solution by multiplying the concentration (concentration) by the activity coefficient (f), which in turn was calculated according to the [3]:

$-\log f = -AZi^2\left(\frac{I^{0.5}}{1+I^{0.5}} - 0.3\,I\right)$ ……….(4)

Where I represent the ionic strength, which was calculated from the Griffin & Jurinak (1973) equation:

I = 0.013 E.C ………..(5)

As E.C represents the electrical conductivity of the solution (deciSemens m-1)

z is the valency of the ion

A represents constant = 0.509 ………(6)

3. Results and Discussion

3.1. Selectivity Coefficient

The ion exchange relationship was studied as a supportive matter in knowing the availability of positive nutritional ions for plants. Studying the state of cationic balance, especially for calcium and sodium, is necessary to predict the aggregation of these ions on the surfaces of the exchange complex and the possibility of washing them to the lower layers and knowing the dominance of any of these ions on the exchange surfaces.

This study occupies a greater amount of importance in the climate conditions of arid and semi-arid regions, as the high evaporation-transpiration contributes to determining the area of dissolution and thus the occurrence of precipitation of calcium carbonate, which pushes towards the dominance of sodium ions in the soil, which adds the role of this ion in affecting the properties of soil. Soil requires drawing appropriate strategies in managing and reclaiming these soils to support the state of irrigated agriculture.

The exchange relationship between calcium and sodium and the extent to which the study soil preferred any of the two ions was studied through the quantitative calculation of the preference coefficient in the ion exchange system according to Gapon (KG) and Vanselow (KV) at the ratios (8:2) and (2:8) sodium Calcium, for concentrations of 100, 200, 400, and 800 $mmol_C\ L^{-1}$. The results showed to favor calcium by binding in the exchange sites compared to the sodium ion change sites compared to the sodium ion, Tables 3 and 4. These results were in line with those of [4] ‹[5] and[6] .

The results also indicated a decrease in the values of the constants (preference coefficient KG and KV) at the ionic ratio (8:2) sodium: calcium compared to the ratio (2:8) sodium: calcium Tables 7 and 8. This may be considered normal due to the low ratio of sodium to calcium (8:2) compared to the ratio (2:8) sodium: calcium, where the ratio was higher for calcium in the first case, while it was higher for sodium in the second case, which generates greater pressure in the equilibrium solution for the element with a higher concentration to bind more with the surface exchange sites compared to the low concentration For the other element, but at the same time when a comparison is made between the two ratios (2:8) and (8:2) sodium: calcium, we find that in both cases the dominance of the exchange sites is for calcium compared to sodium, despite the difference in the above two ratios, and this may be due to the presence of some sites The quality that spreads on the external and internal exchange surfaces tends to bind to this calcium ion on the one hand, in addition to the calcium ion having a double valence that qualifies it to be attracted towards the exchange sites more than in the case of the monovalence carried by the sodium ion on the other hand, and it is taken into account The effect of a factor (dilution - charge) in a soil - solution system that supports an increase in the saturation rate of the exchange complex with a standard calcium ion with a sodium ion to have calcium divalence compared to the monovalence of sodium, but in the case of concentration, vice versa [7].

when studying the effect of increasing the concentration used (100, 200, 400‹ and 800) $mmol_C\ L^{-1}$ on the values of the preference coefficient (KG and KV), this effect differed according to the ratios used (Sodium: Calcium). While the values of the Gapone and Vanselow constants decreased with increasing the concentration used at the ratio of 8:2 sodium: calcium, we find that these values increased with increasing the concentration at the ratio of 8:2 sodium: calcium according to the different soils under study, Tables 39 and 40. This may be due to the fact that At a low level of sodium saturation and an increase in calcium absorption at the edges of the pore structure, it may prevent the free movement of sodium, but at an increase in sodium saturation, the effect of calcium in encapsulation of these sites subsides and disappears, which shows an increase in the preference of sodium for adsorption relatively[8].

The results of the study for the linear relationship between each of the values of the coefficient of preference (KG and KV) and the clay separation at the different soils of the study showed that there is a highly significant negative correlation (r) (-0.878 and - 0.952) at the ratio 8:2 sodium: calcium, respectively, (- 0.855 and -0.923) at the ratio of 8: 2 sodium: calcium, respectively, and there was a significant correlation at the level (0.05) between the preference coefficient (KG and KV) with the electrical conductivity of the saturated soil paste extract and most of the values of the exchange capacity of the positive ions. While no correlation appeared when studying the relationship between the preference coefficient constants (KG and KV) and each of the organic matter and the degree of soil reaction (pH) and lime ($CaCO_3$) Table5 . It is believed that the presence of a highly significant correlation of the clay separation with the values of the preference coefficient indicates an increase in the soil content of clay reduces the speed of the exchange process for the sodium ion, which indicates that the mineral composition of the clay separation may contain specific sites that tend to bind with the calcium ion compared to the sodium ion.

Table 3. Gapon (KG) selectivity coefficients for the concentrations and ratios used

Pedons number	Location	horizon	depth (cm)	Ionic ratio Ca :Na							
				2:8				**8:2**			
				Equilibrium solution concentration(mmole$_c$ liter^{-1})				Equilibrium solutions concentration(mmole$_c$ liter^{-1})			
				100	**200**	**400**	**800**	**100**	**200**	**400**	**800**
P_1	Basra / Al-Shafi	A	0 - 28	0.045176	0.038676	0.029157	0.01722	0.110077	0.219814	0.239911	0.344900
		C_1	28 - 71	0.013802	0.013301	0.012515	0.012009	0.101483	0.211453	0.283901	0.339414
		C_2	113 +	0.073952	0.069591	0.059288	0.047965	0.102977	0.208249	0.384133	0.425162
P_2	Basra/Al-Mashab	A	0 - 21	0.031882	0.030791	0.02839	0.026525	0.118079	0.121217	0.201464	0.205234
		C_1	90 +	0.063857	0.053398	0.035333	0.020863	0.10542	0.241316	0.273196	0.354368
P_3	Thi-Qar/Al Jabayish	A	0-20	0.044329	0.039609	0.036872	0.028978	0.072413	0.133708	0.211118	0.23419
		C_1	20 – 35	0.059185	0.03668	0.034635	0.023381	0.108024	0.109308	0.291575	0.313337
		C_2	35 – 81	0.040202	0.034253	0.031991	0.027725	0.103972	0.207244	0.222803	0.230817
		C_3	+116	0.04101	0.030869	0.02241	0.013139	0.102867	0.176182	0.21432	0.270108
P_4	Thi-Qar/ Alhimar	A	0 - 22	0.022474	0.021819	0.021118	0.020889	0.106288	0.144588	0.223868	0.233913
		C_1	22 - 46	0.060003	0.030932	0.013196	0.015016	0.119853	0.123232	0.202987	0.205939
		C_2	99+	0.04119	0.032832	0.029132	0.016545	0.107316	0.112638	0.22241	0.281543
P_5	Maysan / Aleazim	A	0 - 19	0.013413	0.013123	0.011687	0.010467	0.105546	0.111536	0.136288	0.218306
		C_1	41+	0.057359	0.055231	0.033868	0.026452	0.055108	0.14862	0.205152	0.278382
P_6	Maysan / Al-Musharrah	A	0 - 18	0.042475	0.041139	0.032803	0.031736	0.084912	0.103153	0.213333	0.239232
		C_1	18 - 57	0.023098	0.020189	0.018413	0.015803	0.100403	0.113209	0.149132	0.224042
		C_2	+100	0.025545	0.024605	0.01732	0.014945	0.054770	0.122288	0.186873	0.221357

Table 4. Vanselow (KV) selectivity coefficients for the concentrations and ratios used

Pedons number	Location	horizon	depth (cm)	Ionic ratio Ca :Na							
				2:8				**8:2**			
				Equilibrium solution concentration(mmole$_c$ liter^{-1})				Equilibrium solutions concentration(mmole$_c$ liter^{-1})			
				100	**200**	**400**	**800**	**100**	**200**	**400**	**800**
P_1	Basra / Al-Shafi	A	0 - 28	0.005358	0.004836	0.004117	0.003251	0.017392	0.023188	0.026174	0.030814
		C_1	28 - 71	0.009559	0.005725	0.004246	0.003628	0.016758	0.020129	0.023324	0.024146
		C_2	113 +	0.009658	0.005995	0.004792	0.003794	0.014823	0.018158	0.020766	0.021650
P_2	Basra/Al-Mashab	A	0 - 21	0.003363	0.003192	0.002041	0.002071	0.02241	0.024509	0.031054	0.033430
		C_1	90 +	0.007638	0.004041	0.003884	0.003487	0.012371	0.015042	0.028518	0.030268

P_3	**Thi-Qar/Al Jabayish**	**A**	0-20	0.00449	0.003921	0.003135	0.002313	0.021289	0.030734	0.037555	0.047386
		C_1	20 – 35	0.004952	0.003107	0.003757	0.003445	0.01384	0.020684	0.036113	0.046782
		C_2	35 – 81	0.003756	0.00205	0.002368	0.006362	0.013516	0.015009	0.02598	0.036527
		C_3	+116	0.004081	0.003707	0.003285	0.003275	0.012193	0.014673	0.021464	0.027274
P_4	**Thi-Qar/ Alhimar**	**A**	0 - 22	0.003174	0.002864	0.002808	0.002489	0.024734	0.032364	0.061128	0.064245
		C_1	22 - 46	0.003133	0.002942	0.002931	0.002154	0.024113	0.028224	0.042694	0.05091
		C_2	99+	0.004029	0.003567	0.002933	0.002326	0.016828	0.022345	0.035464	0.033693
P_5	**Maysan / Al - Eazim**	**A**	0 - 19	0.001796	0.001546	0.000934	0.000873	0.022436	0.030098	0.041239	0.048505
		C_1	41+	0.004832	0.002869	0.00284	0.002506	0.015051	0.020741	0.030044	0.031095
P_6	**Maysan / Al-Musharrah**	A	0 - 18	0.003663	0.002596	0.001236	0.001375	0.019101	0.025745	0.03832	0.05548
		C_1	18 - 57	0.002869	0.001639	0.001508	0.00216	0.017677	0.019103	0.034989	0.050386
		C_2	+100	0.002949	0.002272	0.001034	0.000936	0.014652	0.017382	0.030795	0.047009

Table 5. Computation of Regression equations and Correlation coefficients

NO.		8:2 Ca :Na Regression equations	orrelation coefficients	2 : 8Ca:Na Regression equations	Correlation coefficients
1	K_G VS Clay	y = -3388.9x + 538.18	r= -0.878**	y = -1068.8x + 626.81	r= -0.923**
2	K_V VS Clay	y = -32890x + 538.2	r =0.952**	y = -5332.1x + 577.48	r = 0.855**
3	K_G VS EC	y = 0.0003x + 0.0223	r = 0.5021*	y = -0.0011x + 0.2265	r= 0.4703*
4	K_V VS EC	y = 5E-05x + 0.0017	r = 0.7104**	y = 0.0002x + 0.0216	r = 0.5162*
5	K_G VS CEC	y = -0.0007x + 0.0493	r = 0.4076*	y = 0.0034x + 0.1161	r = 0.5665*
6	K_V VS CEC	y = -0.0001x + 0.0059	r= 0.5652*	y = -0.0006x + 0.0419	r= 0.5459*

* Significant at the 5% level
** Significant at the 1% level.

4. Conclusion

The study found a highly significant negative correlation (r) (-0.878 and -0.9516) at the ratio 8:2 sodium: calcium, respectively, for the linear relationship between each value of the coefficient of preference (KG and KV) and the clay separation at the various soils of the study. However, when the selectivity coefficient constants (KG and KV) were compared to the levels of organic matter, soil pH, and lime (CaCO3), no significant relationship was found.

References

[1] USAID, 2003. Strategies for assisting the marsh dwellers and restoring the marshland in southern Iraq. Interim Status report.
[2] Page A L, Miller R H, and Kenney D R. 1982. Methods of Soil Analysis Part (2). 2nd ed. Agronomy 9 Am. Soc. Agron. Madison, Wisconsin.
[3] Delver P. 1962. Saline soils in the lower Mesopotamian plain. Ministry of Agriculture. Iraq. Tech. bull. No:7
[4] Al-Helou M A N. 2001. Thermodynamic trends in describing ion exchange reactions of positive ions in calcareous soils. Master's thesis, College of Agriculture, University of Basra.
[5] Yassin M M. 2010. The effect of the rhizosphere of the date palm Phoenix dactylifera and Sidr Ziziphus spinachriti on some mineral, chemical, physical، and biological properties of some calcareous soils. *.Ph.D* thesis, College of Agriculture, University of Basra.
[6] Ahmed H M, and Yousif EY. 2019. Kinetic Description of Sodium Behavior in some affected and *affected-non* soil by salts. *Mesopotamia Journal of Agriculture,* **47**:139-148.
[7] Ghafoor, A., Hina, K., & Murtaza, G. (2004). Estimation of Gapon exchange coefficient for different textured soils and landforms of Punjab, Pakistan. *Pakistan Journal of Agricultural Sciences,* **41**:25.
[8] Singh B, Srivastava P C, and Srivastava M. 2018. Calcium-Sodium exchange equilibria in *two* soils of Chambal command Area of Rajasthan, India. *Land Degradation & Development,* **29**: 2739-2745.