EFFECT OF ION PAIRS ON DECREASE THE RISK OF USING SALINE WATER FOR IRRIGATION

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ABSTRACT

This investigation was conducted during January, 2018 to April, 2019 to investigate the role of correcting ion pairs and activity in decreasing the risk of saline water for irrigation. The groundwater of (31) wells in Makhmur district were depended in this study .The results indicated that amount of ions contributing in ion pairing was ranged between (0.77 -15.42 mmole l^{-1}) with the mean of 6.56 mmole l^{-1}.and the dominate ion pairs were $(CaSO_4)^0$, $(MgSO_4)^0$,$(MgHCO_3)^+$ and $(CaHCO_3)^+$,with the values of 5.00, 4.50, 2.37 and 1.33 mmolc l^{-1} respectively. The studied saline water in Makhmur district did not suitable for irrigation the soils having low, medium and high permeability, while after correcting ion pairs and activity 14 of the studied saline waters were suitable for irrigation (3 of them for soil having medium permeability and 11 of them for soils having high permeability). It means correcting ion pairs and activity caused removal the risk of 14 saline waters for irrigation or caused decrease the risk of 45% of the studied saline water. Correcting ion pairs and activity caused shifting water class from no suitable for irrigation to suitable for irrigation depending on salinity potential values and Doneen classification.

Keywords: water quality, groundwater, makhmur district, ionic activity

تأثير الأيونات المزدوجة في انخفاض خطورة استخدام المياه المالحه للري

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المستخلص

اجريت هذه الدراسة خلال فترة كانون الثاني 2018 الى نيسان 2019 من اجل دراسة تأثيير الأيونات المزدوجة في تقليل خطورة استخدام المياه المالحة للري. أشارت النتائج ان كمية الأيونات المزدوجة تراوحت بين (0.77–15.42) مليمول شحنة لتر– كانت الأيونات المزدوجة السائدة $(CaSO4)^0$, $(MgSO4)^0$, $(MgHCO3)^+$ and $(CaHCO3)^+$: ان المياه المالحة في منطقة مخمور غير صالحة للري ولكن بعد تعديل الأيونات المزدوجة اصبحت مياة 14 بئرا صالحة للري للترب عالية النفاذية أي ان تعديل الأيونات المزدوجة ازالت خطورة 45% من المياه.

كلمات مفاتحية: نوعية المياه,المياه الجوفية,منطقة مخمور,الفعالية الأيونية

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INTRODUCTION

Groundwater is one of the water resources in Iraqi Kurdistan region and in many semiarid and arid regions. Groundwater has the ability to mobilize and transport soluble salts when it moves through the regolith. It is very important to know the water level and its movements, in particular with respect to rainfall events and different agricultural practices for example irrigation (14). Groundwater caters the agricultural requirement. Some of the ground waters have high EC value or they are saline water at the same time this saline water is using for irrigation by farmer (8). Large quantities of salt are brought into agricultural areas by water of good quality. This salt affects the properties of the soil and the growth of plant. Irrigation of agricultural lands accounted for 70% of the water used worldwide. Water is essential for maintaining adequate food supply and a productive environment for human, animal and plant population. World agriculture consumes approximately 70% of freshwater with drawn per year (22). The area of irrigated land in Kurdistan is increase very slowly because of water shortage for irrigation. Ion pairs defined by Adams (1) as the approaching of some soluble anions and cations to each other for the distance 0.5 nm, and each of them keeps its hydration shell. The ion pairs charge depends upon valence of the contributed anion and cation in ion-pairs. The ion pairs are non-active chemically or they are non-conductive for electric, for this reason they are not available for plants and not contribute in chemical reaction (11). Adams (1) summarized the general principles of ion pairs as follow: There is no ion pairing between chloride and cations. The ion pairing between NO_3^- and cations can be neglected. Ion pairing between SO_4^{-2} and univalent cations is slight but it's extensive with multivalent cations. Ion pairing between $H_2PO_4^-$ and HPO_4^{-2} can be neglected with univalent cations, while it's significant with multivalent cations but not extensive. Ion pairing between HCO_3^- and univalent cations is significant. After having addressed the formation of both ion pairs and complexes, it is necessary to reconsider how to calculate ion activities from measured total concentrations. Activity is linked to concentration via activity coefficient as described by (10).

$a=\gamma * c$…………………… (1) Where:

a= activity. γ=Activity coefficient. C = concentration (mol L^{-1}). In general increase in sanity or EC of ground water causes increase in formation of ion pairs (11). There are some studies in Kurdistan region about the amount of ions contributing in ion pairing (11, 19, 6, and 2). The ion pairs and ion activity depended on ionic composition of water (16 and 9). On the other hand ion pairing and activity effects on water class especially in saline water. Esmail and Salih (10) indicated to classification of 38 ground waters in Erbil plain, correcting ion pairs and activity only affected on 3 water samples depending on salinity potential, means correcting ion pairs and activity affected on conversion of 5 water samples towards the better class 3 of them changed from bad class to moderate class and 2 of them changed from moderate to good class) which salinity of them ranged between (2.45 - 5.65) dS m^{-1}. While the 33 ground water samples were not affected by correcting ion pairs and activity due to low salinity of them or most of them was non saline water. On the other hand correcting ion pairs and activity may have –ve effect on classification but this effect is very low in our country due to low initial SAR value of water (2 and 17). Alani (2) noticed the role of correcting ion pairs and activity in conversion water classes but in low rate due to low EC value of the studied waters. There are numerous global systems of irrigation water classification, but the classification which are affecting by correcting ion pairs and activity, when depend on Sodium adsorption ratio (SAR), Salinity potential (SP) and residual sodium carbonate (RSC). Since there are no studies directly on the role of ion pairs and activity in decrease the risk of saline water for irrigation for this reason this study was selected to test the role of correcting ion pairs and activity in decreasing the risk of saline water for irrigation. On the other hand the water quality in Iraq was studied by many researchers, such as (21) studied water quality for main rivers in Iraq for irrigation purpose. Salman and Joubory (20) studied the combination effect of water quality and bio fertilizers in some chemical properties of the soil at Abu-Ghraib. Alhadithi and Hassan (3) studied the ground water quality in western part of Iraq he indicated to more water suitable in central part and to word the south-west. Hassan (12) investigated the effect off irrigation water quality and tillage systems on some soil properties.

MATERIALS AND METHODS

a- Water sampling: The water samples were taken from 31 wells in Makhmur district during April, 2018 to April, 2019 the depth of wells ranged from (150-200) m.

b- Water chemical analysis: The chemical properties of water samples (EC, pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-} and SO_4^{2-}) were determined according to APHA (4) as shown from Table 1

c- Determination of Ion pairs: Determined according to (15).

d- Sodium adsorption ratio (SAR), Salinity potential (SP) and Residual sodium carbonate (RSC) ($mmolc.l^{-1}$) values were calculated as follow:

$SAR = (Na^{+} / [SQR\ (Ca^{2+}+Mg^{2+}) / 2]$ .... (2)

$(SP) = (Cl^{-} + ½\ SO_4^{2-})$ ………. (3)

$RSC= (CO_3^{2-}+HCO_3^{-}) - (Ca^{2+}+Mg^{2+})$ ……….(4)

Doneen (7) classified water depending on (SP) and soil as follow:

Water quality	Salinity potential (SP) = (Cl^{-} + 1/2 SO_4^{2-}) $mmol_c\ L^{-1}$		
	High	Moderate Permeability	Low
Good	< 7	< 5	< 3
Moderate	7-15	5-10	3-5
Bad	> 15	> 10	> 5

Wilcox (23) classified the irrigation water into three classes depending on residual sodium carbonate (RSC) as follow:

Water class	RSC ($mmol_c\ L^{-1}$)
Probably safe	< 1.25
Marginal	1.25-2.5
Unsuitable	> 2.5

Ayres and Westcot (5) classified irrigation water depending on EC_{iw} and SAR as follow:

Potential irrigation problem	Unit	Degree of restriction use		
		None	Slight to moderate	Severe
EC_{iw} at 25 °C	$dS\ m^{-1}$	< 0.7	0.7-3.0	> 3.0
SAR		< 3	3-9	> 9

Table1. shows the locations and some chemical properties of the studied waters

Locations	EC dS m^{-1}	pH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl⁻	SO_4^{--}
			Concentration ($mmol_c L^{-1}$)						
Serma (W1)	5.19	6.70	20.40	6.60	25.23	0.16	3.40	2.20	46.79
Pwngina (W2)	3.73	7.20	26.40	8.00	26.24	0.11	2.80	0.50	57.45
Qalata Soran (W3)	4.10	7.30	19.00	16.00	10.32	0.21	13.00	12.80	20.73
Qwcha Spilka (W4)	5.26	7.20	24.00	11.00	20.42	0.21	13.20	15.00	30.93
Grdachal (W5)	5.51	7.20	29.60	11.40	14.31	0.11	12.80	21.70	25.92
Grdi gwm (W6)	4.18	7.60	27.20	9.80	7.25	0.27	8.20	10.00	22.32
Grdbasha Sabir(W7)	3.40	7.00	25.40	8.80	6.43	0.23	3.40	10.70	26.46
Qalata Soran (W8)	4.50	7.10	24.00	16.00	8.34	0.21	2.60	10.20	35.85
Maxmur (W9)	5.60	7.20	25.80	20.20	18.20	0.36	12.80	14.20	36.56
Qasran (W10)	3.09	7.00	26.80	9.20	19.18	0.34	3.20	0.60	51.72
Gwl Gamesh (W11)	5.45	6.20	24.60	20.40	10.39	0.23	3.20	11.10	41.32
Kandal Yrmja (W12)	4.83	7.10	21.20	14.80	10.28	0.11	10.00	14.40	22.09
Said Obid (W13)	2.10	8.10	3.00	1.00	36.33	0.14	2.80	0.70	36.97
Mala Qara (W14)	2.23	7.50	6.80	3.20	34.31	0.11	4.00	0.70	39.72
Grdi Gum (W15)	3.12	7.40	10.20	5.80	30.28	0.09	3.80	1.10	41.47
Shora zartka (W16)	2.16	7.60	2.20	0.80	31.29	0.14	4.60	0.60	29.23
Chagha Mera(W17)	4.43	8.10	18.40	8.60	28.26	0.25	2.40	1.70	51.41
Chl Haweza (W18)	2.20	8.10	6.60	3.40	37.34	0.09	4.00	0.50	42.93
Qwra Gor (W19)	4.40	7.59	14.20	7.60	16.55	1.09	3.30	11.8	24.34
Gabalak 2 (W20)	2.82	7.42	10.41	8.29	9.39	0.09	2.67	7.10	18.41
Gabalak 3 (W21)	2.85	7.48	10.56	11.46	6.43	0.08	2.64	3.20	22.70
Gabalak 1 (W22)	3.03	7.41	11.28	8.38	10.54	0.08	2.76	7.54	19.98
Gabalak 4(W23)	3.15	7.55	9.88	11.47	10.10	0.10	2.83	7.81	20.91
Grdachal Qaraj1(W24)	7.04	7.56	25.45	22.51	22.02	0.44	2.18	21.90	46.34
Grdachal Qaraj (W25)	7.75	7.40	23.94	21.47	30.08	0.22	1.94	33.14	40.63
Grdachal , Qaraj (W26)	7.70	7.39	35.26	26.41	10.04	0.26	11.97	23.97	37.03
Grdachal qaraj(W27)	7.63	7.49	26.44	34.71	11.01	0.15	22.63	42.35	27.63
Gabalak 2 (W28)	2.45	7.62	5.53	5.48	13.30	0.11	17.16	5.63	0.55
Dwshewan(W29)	2.59	7.08	12.43	10.58	2.02	0.13	5.38	1.86	18.36
Makhmur(W30)	4.92	7.19	18.19	15.56	17.55	0.13	3.57	11.47	31.57
Chakhamera(W31)	5.65	7.52	16.68	14.58	30.05	0.15	3.02	4.39	50.16

RESULTS AND DISCUSSION

Results in Table 2 show the range and mean for ion concentration, activity and amount of ions contributed in ion paring in the studied water samples. In general increasing the concentration of ions and electrical conductivity caused increase in amount of ions contributed in ion pairing and then decrease in activity of ions. The dominate ions in the most waters (81%) of the studied area were Mg and SO_4, it means having Mg-SO_4 family due to the Fars formation of the studied area (13), while the water of 6 wells having Ca-SO_4 family. For these reasons the series of ions contributed in ion paring were arranged dissentingly as follow: SO_4 > Ca > Mg > HCO_3 > Na > K. The contributing ions in ion pairing especially in saline water decrease the risk of salinity since ion pairs cannot absorb by plant roots or they are not active (8). For this reason the classification of saline water depending on salinity potential (SP) and sodium adsorption ratio (SAR) for irrigation after correcting ion pairs regards as a most important issue.

Table 2. shows ranges, and means for some studied characters and amount of ions contributed in ion pairs

ions	Concentration			Activity			Amount of ions contributing in ion pairs		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Ca^{2+}	2. 20	35.26	18.12	2.20	35.26	18.00	0.22	6.33	3.35
Mg^{2+}	0.80	34.71	12.05	0.80	34.71	12.05	0.11	6.33	2.25
Na^{+}	2.02	37.34	18.18	2.02	37.34	18.18	0.09	2.20	1.27
K^{+}	0.08	1.09	0.21	0.08	1.09	0.21	0.01	0.05	0.02
HCO_3^{-}	1.94	22.63	6.20	1.94	22.63	6.20	0.20	4.33	1.29
SO_4^{-2}	0.55	57.45	32.85	0.44	33.90	18.83	0.23	10.65	5.63
Cl^{-}	0.20	42.35	9.96	0.20	42.35	9.96	0.0	0.0	0.0
CO_3^{-}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
pH	7.10	8.10	7.42	7.10	8.10	7.42	-	-	-
EC	2.10	7.75	4.29	2.10	7.75	4.29	-	-	-

Results in Table 3 explain the type of ion pairs and their amount in the studied well waters, which ranged between (0.77 - 15.42 mmole l^{-1}) with the mean of 6.56 mmole l^{-1}. It is appear that large amount of ions contribute in ion paring which causes decrease in osmotic positional then shifting the non-suitable water for irrigation to suitable or decrease the risk of using saline water for irrigation especially waters having Ca-SO_4. Ca-HCO_3, Mg-SO_4, and Mg-HCO_3 families. Table 4 and 5 Explain that correcting ion pairs and activity were not affected on change the water classes depending on SAR due to low contributing of sodium in ion pairing and low increase in SAR value (1.01 - 1.28) times which not caused change in water classes depending on (18) classification (8). For this reason in both cases water of 26 wells were suitable for irrigation and water of 5 wells were not suitable or having sever restriction (Table 4).

Table3. Types and amount of ion pairs for the studied waters

Ion pairs	Amount of ion pairs (mmol L^{-1}) Minimum	Maximum	Mean
$(CaHCO_3)^+$	0.06	1.33	0.34
$(CaSO_4)^o$	0.16	5.00	3.01
$(MgHCO_3)^+$	0.05	2.37	0.90
$(MgSO_4)^o$	0.06	4.50	1.35
$(KSO_4)^-$	0.008	0.01	0.01
$(KHCO_3)^o$	0.0 07	0.01	0.01
$(NaHCO_3)^o$	0.03	0.90	0.04
$(NaSO_4)^-$	0.06	1.30	0.90
∑	0.77	15.42	6.56

The results indicated that 84% of the studied waters were suitable for irrigation and16% of the studied water were not suitable for irrigation (5).

Table 4. Water classes before and after correcting ion pairing and activity

Water classes depending on SAR values (Before correcting)			Water classes depending on SAR** values (After correcting).		
No restriction	Low- moderate restriction	Sever restriction	No restriction	Low- moderate restriction	Sever restriction
10	16	5	10	16	5

Results in Table 5 refers to decrease in salinity potential after correcting ion pairs and activity (SP**) results in Table 6 Explains the effect of correcting ion pairs and activity on decrease in saline water risk depending on Doneen (7) due to shifting most of the studied saline water from bad class to moderate class for high permeable soils such as soil in Makhmur district. Correcting ion pairs and activity caused high decrease in salinity potential of the studied waters depending on their chemical composition as shown from Table 5 which caused shifting the water classes from bad to moderate or suitable water for irrigation Table 6, it means correcting ion pairs and activity caused decrease in the risk of using saline water for irrigation purpose. It is clear from Table 6 that all the studied saline water in Makhmur district were not suitable for irrigation for the soils having low, medium and high permeability, while after correcting ion pairs and activity 14 of the studied saline waters were suitable for irrigation 3 of them for soil having medium permeability and 11 of them for soils having high permeability). It means correcting ion pairs and activity caused removal the risk of 14 saline waters for irrigation or caused decrease the risk of 45% of the studied saline water. Similar results were recorded by (10), for some samples of saline water in Erbil plain. The results were referring to the necessity of focusing on ion paring in saline waters. Results in Table 5 explains decrease in negative value or RSC after correcting ion pairs, while correcting ion pairs and activity not caused change in water classes depending on RSC values due to high concentration of Mg and Ca in the studied waters (11). The results indicated to the dominancy of $(CaSO_4)^0$, $(MgSO_4)^0$, $(MgHCO_3)^+$ and $(CaHCO_3)^+$ ion pairs in the studied waters. The increase in ion pairing with increase in salinity of waters then decreases the risk of using saline waters for irrigation purpose. The ion pairing caused shifting the bad water class to moderate or suitable water for irrigation. It is necessary to focus on ion pairing in studying saline water for irrigation purpose in the future studies on water quality and classification.

Table5. Effect of correcting ion pairing and activity on SAR and SP values

Table6. Effect of ion pairing and activity on decrease in risk of saline water in Makhmur district

Water	SAR	SAR**	SAR**/SAR	SP	SP**	SP**/SP	RSC	RSC**	RSC**/RSC
(W1)	6.87	7.97	1.16	25.60	14.13	1.81	-23.60	-13.95	1.69
(W2)	6.33	7.29	1.15	29.23	15.44	1.89	-31.60	-20.28	1.56
(W3)	2.47	2.63	1.07	23.17	29.75	0.78	-22.00	-16.70	1.32
(W4)	4.88	5.63	1.15	30.47	20.91	1.46	-21.80	-13.25	1.65
(W5)	3.16	3.66	1.16	34.66	30.83	1.12	-28.20	-15.37	1.83
(W6)	1.69	2.04	1.21	21.16	16.70	1.27	-28.80	-15.29	1.88
(W7)	1.55	1.78	1.14	23.93	18.51	1.29	-30.80	-18.98	1.62
(W8)	1.86	2.17	1.16	28.13	20.42	1.38	-37.40	-22.96	1.63
(W9)	3.79	4.38	1.16	32.48	24.44	1.33	-37.40	-20.09	1.86
(W10)	4.52	5.20	1.15	26.46	14.05	1.88	-32.80	-19.62	1.67
(W11)	2.19	2.61	1.19	31.76	22.47	1.41	-41.80	-25.70	1.63
(W12)	2.42	2.92	1.21	25.45	20.70	1.23	-26.00	-14.19	1.83
(W13)	25.69	26.22	1.02	19.19	10.87	1.77	-1.20	-1.01	1.19
(W14)	15.34	15.56	1.01	20.56	11.43	1.80	-6.00	-4.57	1.31
(W15)	10.71	10.83	1.01	21.84	11.88	1.84	-12.20	-9.57	1.27
(W16)	25.14	25.55	1.01	15.22	8.79	1.73	1.60	1.00	1.60
(W17)	7.69	7.97	1.04	27.41	15.84	1.73	-24.60	-17.65	1.39
(W18)	16.70	16.38	0.98	21.97	12.52	1.75	-6.00	-4.91	1.22
(W19)	5.01	5.22	1.04	23.97	19.10	1.25	-18.50	-14.17	1.31
(W20)	3.07	3.24	1.05	16.31	12.72	1.28	-16.03	-12.54	1.28
(W21)	1.94	2.08	1.07	14.55	10.24	1.42	-19.38	-15.28	1.27
(W22)	3.36	3.59	1.07	17.53	13.84	1.27	-16.90	-13.15	1.29
(W23)	3.09	3.26	1.05	18.27	14.29	1.28	-18.52	-14.86	1.25
(W24)	4.50	5.10	1.13	45.07	33.95	1.33	-45.78	-28.51	1.61
(W25)	6.31	7.08	1.12	53.46	43.91	1.22	-43.47	-27.07	1.61
(W26)	1.81	2.25	1.25	42.49	34.16	1.24	-49.70	-24.95	1.99
(W27)	1.99	2.56	1.28	56.17	50.23	1.12	-38.52	-17.37	2.22
(W28)	5.67	6.37	1.12	5.91	5.85	1.01	6.15	4.29	1.43
(W29)	0.60	0.70	1.18	11.04	7.37	1.50	-17.63	-11.51	1.53
(W30)	4.27	5.10	1.19	27.26	19.99	1.36	-30.18	-17.53	1.72
(W31)	7.60	8.27	1.09	29.47	17.43	1.69	-28.24	-17.35	1.63
Mean	6.68	6.62	1.19	26.45	30.03	1.34	-23.97	-14.94	1.60
Max.	25.69	26.22	1.28	56.17	50.23	1.89	-49.70	-28.51	2.11
Min.	0.60	0.70	0.98	5.91	5.80	0.78	-1.20	-1.00	1.19

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