SOME CATIONS MOVEMENT IN CALCAREOUS SOIL COLUMNS UNDER EFFECT OF SALINE WATER MIXED WITH HUMIC ACID

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ABSTRACT

A laboratory experiment was conducted to study the impact of humic acid with different levels of saline water on the movement of Sodium, Calcium and Magnesium, and the kinetics of Sodium adsorption ratio in calcareous soil with a texture clay loam using the mixing displacement techniques. The soil was taken from the surface layer (0-30 cm), air dried and passed through a 2 mm diameter sieve. It was filled in columns of polyethylene. A fixed column of water was placed above the surface of the soil column of different salinity water (0.72, 3.00, 5.00 and 7.00 dSm^{-1}), in accordance with humic acid levels of 0.00, 0.25 and 0.50 g L $^{-1}$. The process of washing and collecting leachate continued daily. The amount of Sodium, Calcium and Magnesium in the water filtered over time. The results showed that the amount of Sodium released increases with the levels of added humic acid and any levels of saline water used. The amount of Calcium and Magnesium released decreases with time and increases the added levels of the humic acid and any levels of saline water used. Diffusion equation is the best equation described the movement of salt.

Keywords: humic acid, saline water. sodium adsorption ratio, diffusion equation, cations complexes

مجلة العلوم الزراعية العراقية- 2019 :50(5):1313-1323 الحديثي وآخرون

حركة بعض الايونات الموجبة في اعمدة تربة كلسية تحت تاثير المياه المالحة المخلوطة بحامض الهيوميك

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المستخلص

اجريت تجربة مختبرية لدراسة تأثير حامض الهيوميك المضاف خلطاً الى مياه مختلفة الملوحة في حركة الصوديوم والكالسيوم والمغنيسيوم وحركيات نسبة امتزاز الصوديوم في تربة كلسية ذات نسجةمزيجة طينية بأستخدام تقنيات الازاحة الامتزاجية. اخذت تربة من الطبقة السطحية (0 – 30 سم) جففت هوائياً ومررت عبر منخل قطر فتحاته 2 ملم وعبأت في اعمدة من البولي اثلين الصلب. سلط عمود ماء ثابت فوق سطح عمود التربة من المياه مختلفة الملوحة وهي 0.72و3.00 و5.00 و7.00 ديسيسيمنز م$^{-1}$ وبالتوافق مع مستويات حامض الهيوميك وهي 0.00 و 0.25 و0.50 غم لتر$^{-1}$. واستمرت عملية الغسل وجمع الراشح يومياً . قدر الصوديوم والكالسيوم والمغنيسيوم في المياه المترشحة مع الزمن. بينت النتائج ان كمية الصوديوم المتحررة تزداد بزيادة مستوبات حامض الهيوميك المضاف ولأي مستوى من مستويات المياه الملحية المستعملة وان كمية الكالسيوم والمغنيسيوم المتحررة تقل مع الزمن وبزيادة مستويات الاضافة من حامض الهيوميك ولأي مستوى من مستويات المياه الملحية المستعملة. ان احسن معادلة من معادلات الحركية المستخدمة لوصف نسبة امتزاز الصوديوم هي معادلة الانتشار.

كلمات مفتاحية: حامض الهيوميك، مياه مالحة، نسبة امتزاز الصوديوم، معادلة الانتشار. معقدات الكاتيونات

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INTRODUCTION

According to data released by the Food and Agriculture Organization (FAO), 69% of the water consumed in the world which used in agriculture, and the area used for irrigation water will increase by 25-30% in 2025 (10) Therefore, Continuous demand for fresh water, such as brackish water, drainage water and shallow salt wells (2, 16, and 17). This is faced by an increase in risk such as soil salinization and reduction of yield. Irrigation water is one of the main sources of salt accumulation in the soil. This depends on the amount of salts transported by the water and the high temperature that increases the evaporation process, which increases their accumulation continuously in the soil. The concentration of salts in the root zone affects the growth and development of the plant through the lack of water absorbed by the roots of the plant and imbalance in the ions (13 and 25). The most important way to development and organized water use is to exploit saline water by reducing its chemical and physical effect (6). The humic acid is characterized by its high ability to chelating dissolved ions in the soil solution and to form organic complexes to contain the active groups such as carboxylic ($COOH^-$) and phenol (OH^-), which control the electrochemical behavior of the humic acid and they are a major cause of adsorption, cation exchange, complexes and chelating (21). These complexes facilitate their movement and washing with irrigation water, which affects the concentration of ions in the soil solution and the Sodium adsorption ratio, in addition to its high ability to improve the of physical soil properties such as structure, increase permeability and increase the speed of moving (12, 15and 22). Organic complex made by Sodium are more soluble and easier to wash than soil compared with the complexes of Calcium and Magnesium (23). The process of chelating and complex configuration follows the following order $Ca^{+2} < Mg^{+2} < K^{+1} = NH4^{+1} < Na^{+1}$ (19). The process of chelating of cations by humic acid occurs through the ion exchange process between the ions found in the soil solution and the ions that are absorbed on the humic acid and the organic complexions are formed by forming cationic bridges with the humic acid of the direct or indirect processes of the chelating (12). The base cations (Na^+, K^+, Ca^{++} and Mg^{++}) are held by the humic acid through simple ion exchange with the groups of carboxylic and the composition of groups (RCOONa and RCOOK) (24). Several studies have explained the effect of humic acid in chemical soil properties such as Calcium, Magnesium, Sodium and Sodium adsorption ratio. Ali and Wanti (4) found that the addition of humic acid levels of 0.889, 1.778, 2.667, and 3.556 g kg^{-1} soil in liquid form to clay soil resulted in reduced Sodium values in soil solution. The exchange of salt cations with hydrogen in the carboxyl and hydroxyl groups in addition to the improvement of porosity of the soil, which encouraged the washing process of the ions that have become complex with the humic acid. (14) found in a field experiment that the addition of humic acid at level (75, 150 and 225) mg L^{-1} mixed with drip irrigation water with electrical conductivity 1.89 dS m^{-1} and Sodium adsorption ratio 5.35 to sandy soil 2.85 dS m^{-1} and the exchangeable Sodium percentage 3.46 significantly reduced the percentage values of Sodium exchange in the soil compared to the non-additive treatment. The aim of this study is to find out the effect of mixed levels of humic acid with different saline water in cations released and Sodium adsorption ratio in column of calcareous soil.

MATERIALS AND METHODS

A laboratory experiment was carried out at the university of Baghdad laboratories. An alternative site of Anbar university, saline water brought from a nearby drainage canal to the college of agriculture with its electrical conductivity 8.2 dS m^{-1} In the process of blending with the river water (0.72 dS m^{-1}) to make 3.00(S2), 5.00(S3) and 7.00(S4) dS m^{-1} saline water. The blending process was carried out by using saline water with concentrations of the humic acid (0.00(HA0), 0.25(HA1) and 0.50(HA2) g L^{-1}). Soil surface brought from the depth of 0-30 cm. Soil was dried and passed through a 2 mm diameter sieve. It was filled in columns of polyethylene, 7.5 cm in diameter, 30 cm high and the bulk density 1.37 Mg m^{-3}. Placed a filter down the column 5 cm high of sand and glass wool. Moisten all columns using the capillary property to maintain homogeneity of moisture content throughout the column. The columns were used to study the movement and distribution of salts (4 x 3 = 12 columns). A fixed column of water was placed above the top of the soil column for saline water (0.72, 3.00, 5.00 and 7.00 dS m^{-1}) in agreement with the humic acid levels. The washing process continued until the electrical conductivity of the added water was equal to the electrical conductivity of the filtered water from the columns by collecting the proposed amount of columns and measuring the volume of the each columns filtered daily. Determination of the concentration of cations (Na^+, Ca^{++}, and Mg^{++}) and the Sodium adsorption ratio in the filtrate solution were measured in the filtrate with time. Table 1 shows soil characteristics and table 2 shows the characteristics of water used in the experiment.

The kinetic equations used in the study

Mathematical and physical equations with experimental bases and kinetic chemistry were used to describe the Sodium adsorption ratio in leachate with time (9 and 19).

These equations are:

1- Zero order eq. Ct = C0 – Kt

2 - First order eq. in Ct = in C0 – Kt

3- Second order eq. 1 / Ct = 1 / C0 + Kt

4-diffusion eq. Ct = C0 - $Kt^{1/2}$

5- Elovich eq. Ct = C0 - K lnt

Representing:

C0 = SAR in leachate at zero time

Ct = SAR in the leachate at the specified time

K = rate constant reaction (release constant) SAR

To determine the most efficient SAR formula, the following indicators were adopted:

Selection factor (R^2)

Stander Error of Estimate (SEe)

T table value (variance between values)

RESULTS AND DISCUSSION

Concentration of Sodium **released with time (mmol L^{-1})** : Figure 1 shows the relationship between the total Sodium values mmol L^{-1} released from soil columns by the effect of water of different salinity levels under the influence of different levels of humic acid with time (day). It is observed that Sodium concentrations are increased with time as the levels of the humic acid increase. When using river water 0.72 dS m^{-1} with different levels of humic acid (0.00, 0.25 and 0.50) g l^{-1}. The highest values within 25 days were 245.74, 304.86 and 334.75 $mmol^{-1}$ respectively. The lowest values of Sodium released at 1 day were 4.25 and 6.90 and 9.20 $mmol^{-1}$ respectively. Sodium concentrations released when using salted irrigation water 3.00 dS m^{-1} (S2)with different levels of humic acid (0.00, 0.25 and 0.50) g L^{-1} was the highest value at 25 days (846.52, 968.36 and 1128.16) $mmol^{-1}$ respectively, while the lowest value of Sodium released at 1 day were (3.86, 4.20 and 5.60) $mmol^{-1}$ sequentially. Sodium salts when used with salted water 5.00 dS m^{-1} (S3) with different levels of humic acid (0.00, 0.25 and 0.50) g L^{-1} highest value at 25 day were (998.51, 1197.53 and 1268.01) $mmol^{-1}$ respectively. While the value of Sodium released at 1 day were (9.04, 9.15 and 10.54) $mmol^{-1}$ respectively. The release of Sodium with water of 7.00 dS m^{-1} (S4) with different levels of humic acid (0.00, 0.25 and 0.50) gL^{-1} was the highest value at 25 day (1062.55, 1263.19 and 1394.19) $mmol^{-1}$ in succession. The lowest value of Sodium released at 1 day 5.39 and 7.09 and 7.70 mmol L^{-1} respectively. It could be concluded that the concentrations of Sodium from the soil columns increase by increasing the level of salinity of the water when adding the humic acid and decrease with the addition of the acid of the humic to all levels of salinity of the water. The amount of released Sodium increases to (245.74, 846.52, 998.51 and 1062.55) $mmol^{-1}$ with increasing salinity of water (0.72, 3.00, 5.00 and 7.00) dS m^{-1} respectively and the humic acid is not added (HA0) to the water. The released Sodium concentrations are increased to (304.86, 968.36, 1197.53 and 1263.19) $mmol^{-1}$ for the same saline water levels respectively, with 0.25 g L^{-1} (HA1) humic acid. While Sodium concentrations increased to (334.75, 1128.16, 1268.01 and 1394.19) $mmol^{-1}$ at the addition of humic acid in 0.50 g L^{-1} (HA2) for the levels of salinity of water respectively.

Table 1 Some chemical and physical properties of soil used

Property	the value	measuring unit
EC_e	3.12	dS m^{-1}
pH	7.39	—
SAR	3.69	—
Carbonate minerals	269.00	gm kg^{-1}
Gypsum	2.00	gm kg^{-1}
Organic matter	10.70	gm kg^{-1}
Bulk Density	1.37	Mg m^{-3}
Dissolved ions		
Ca^{2+}	7.12	mmol L^{-1}
Mg^{2+}	5.10	mmol L^{-1}
Na^{+}	12.90	mmol L^{-1}
K^{+}	0.48	mmol L^{-1}
SO_4^{2-}	3.64	mmol L^{-1}
Cl^{-}	11.40	mmol L^{-1}
HCO_3^{-}	3.03	mmol L^{-1}
CO_3^{2-}	Nil	mmol L^{-1}
Soil Separates		
Sand	300	gm kg^{-1}
Silt	330	gm kg^{-1}
Clay	370	gm kg^{-1}
Texture	Clay loam	—

Table 2 some chemical properties of the water used in the experiment

Property	measuring unit	Water salinity levels			
		River water	S_2	S_3	S_4
EC	dS m^{-1}	0.72	3.00	5.00	7.00
pH	—	7.81	7.50	7.40	7.40
Ca^{2+}	mmol L^{-1}	1.89	3.75	6.25	8.75
Mg^{2+}	mmol L^{-1}	1.62	5.00	10.00	13.00
Na^{+}	mmol L^{-1}	4.53	14.0	29.0	35.0
K^{+}	mmol L^{-1}	0.08	0.09	0.10	0.13
Cl^{-}	mmol L^{-1}	1.94	15.00	27.50	35.00
SO_4^{2-}	mmol L^{-1}	0.81	10.00	18.60	28.50
HCO_3^{-}	mmol L^{-1}	0.75	2.50	3.00	4.50
SAR	—	2.42	4.73	7.19	7.50

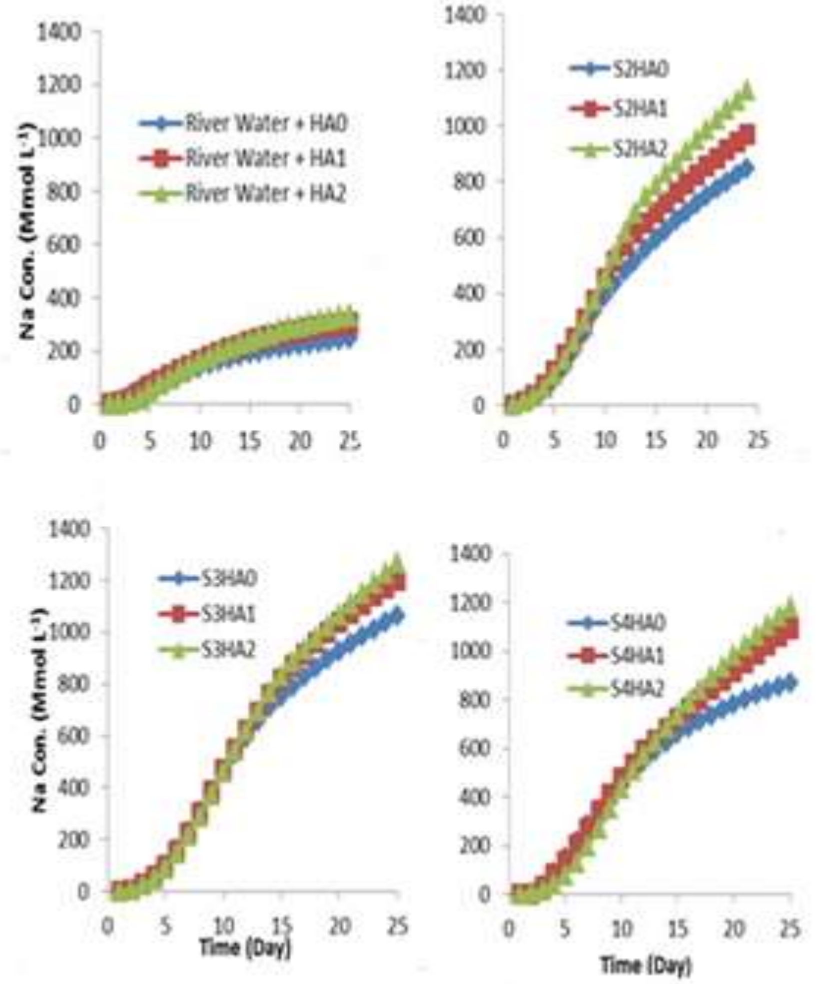

Figure 1. The relationship between Na^{+1} released from water at different salinity levels mixed with different levels of humic acid with time (day).

The increase in Sodium concentrations released with increased levels of the acid is due to Humic acid contains active groups such as carboxyl and hydroxyl, which act on the complex and complex of Sodium ions, forming easy and soluble organic compounds, increasing the washing process (20 and 21).

Concentration of Calcium released with time (mmol L^{-1}).

Figure 2 shows the relationship between total Calcium values (mmol L^{-1}) released from soil columns by the effect of water of different salinity levels and under the influence of different levels of humic acid with time (day). It is observed that Calcium concentrations are reduced over time with increased levels of the humic acid. When using river water of 0.72 dS m^{-1} with different levels of humic acid (0.00, 0.25 and 0.50) g l $^{-1}$, the highest value at 25 day (201.58, 163.49 and 107.35) mmol l $^{-1}$ sequentially. The lowest value of Calcium released at 1 day (12.5, 11.00 and 10.00) mmol^{-1} sequentially. Calcium concentrations released when using salted water 3.00 dS m^{-1} (S2) with different levels of humic acid (0.00, 0.25 and 0.50) g L $^{-1}$ (HA2) was the highest value at 25 day (662.205, 608.99 and 514.335) mmol^{-1} sequentially. While the value of Calcium released at 1 was (8.75, 7.00 and 4.95) mmol^{-1} respectively. Calcium concentrations were released when using salted irrigation water 5.00 dS m^{-1} with different levels of humic acid (0.00, 0.25 and 0.50) g L^{-1} highest value at 25 day (679.561,627.46 and 567.55) mmol^{-1} sequentially, while the lowest value of Calcium released at 1 day was (12.65, 12.58 and 10.15) mmol^{-1} sequentially. Calcium concentrations were released when using irrigation water of 7.00 dS m^{-1} with different levels of humic acid (0.00, 0.25 and 0.50) g L^{-1} (HA2) highest value at time 25 days (849.85, 800.63 and 746.355) $mmol^{-1}$ sequentially.

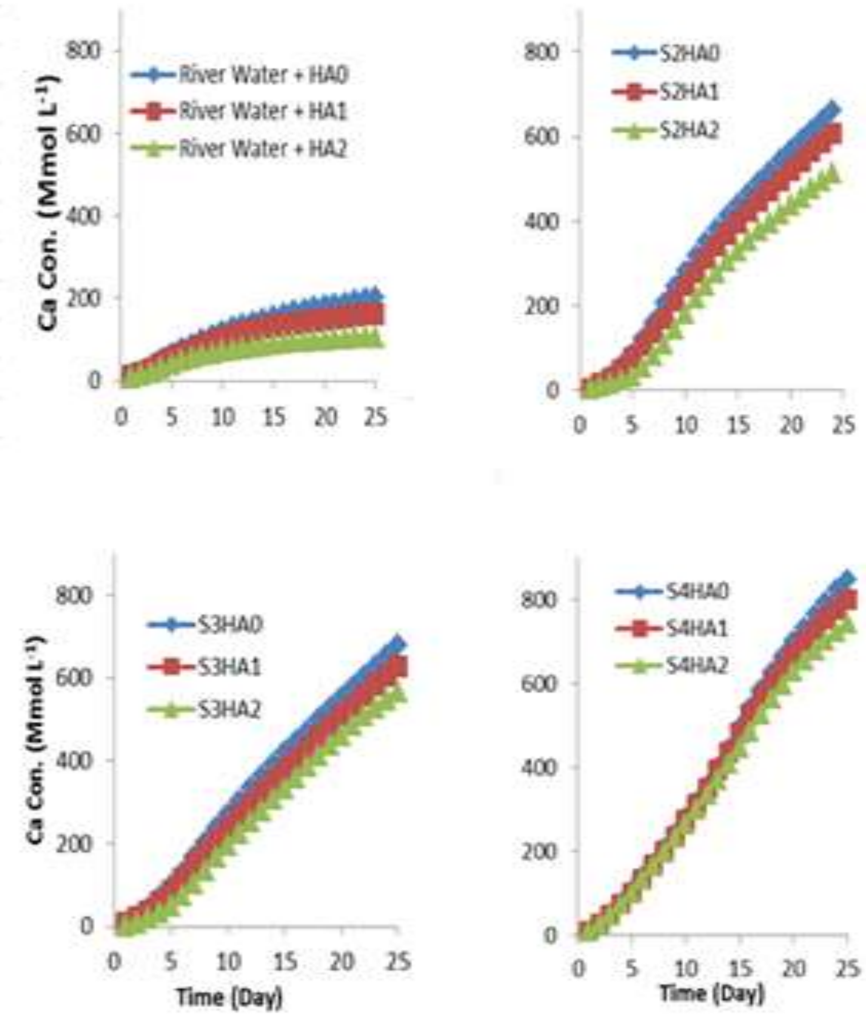

Figure 2. The relationship between Ca^{++} released from water at different salinity levels mixed with different levels of hmic acid with time (day)

It is concluded that the total Calcium concentrations released from the soil columns increase by increasing salinity of irrigation water used when the acid is not added and reduced with increasing levels of humic acid addition, for all salinity levels of irrigation water. The release amount of Calcium increases to (201.58, 662.205, 679.561 and 849.85) $mmol^{-1}$ with increased level of salinity of saline water levels (0.72, 3.00, 5.00, 7.00) dS m^{-1} sequentially, and when the acid is not added to the water. The release Calcium concentrations were reduced to (163.49, 608.99, 627.46 and 800.63) $mmol^{-1}$ respectively for the same saline levels with 0.25 g L^{-1} humic acid. Also, the Calcium concentration release were reduced to (107.35, 514.335, 567. 55 and 746.355) $mmol^{-1}$ when the addition of humic acid at 0.50 g l^{-1} (HA2) and for successive salinity levels. The reduction of release Calcium concentrations with increased levels of humic acid is due to the containment of humic acid on the active groups such as carboxyl and hydroxyl, which acts on the complexity and complexity of Calcium ions and the formation of low mobility organic complexes, which reduces the washing process (23 and 24).

Concentration of Magnesium released with time (mmol L^{-1})

Figure 3 shows the relationship between the values of total Magnesium (mmol L^{-1}) released from the soil columns by the effect of water of different salinity levels and under the influence of different levels of humic acid with time (day). It is observed that the concentration of Magnesium released over time decreases with increasing levels of the humic acid. When using river water 0.72 dS m^{-1} with different levels of humic acid(0.00, 0.25 and 0.50) g L^{-1}) the highest value at 25 day (116.22, 88.59 and 70.79) $mmol^{-1}$ sequentially; the value of Magnesium released at 1 day was 12.40, 7.50 and 6.00 $mmol^{-1}$ in sequence. The concentration of Magnesium released in the use of salted water is 3.00 dS m^{-1} (S3) with different levels of humic acid (0.00, 0.25 and 0.50) g L^{-1}, the highest value at time 25 days (364.29, 313.87 and 297.50) mmol-1 Sequentially. While the value of Magnesium released at 1 day was (7.25, 5.00 and 4.37) $mmol^{-1}$ respectively. The concentration of Magnesium when using saline water of 5.00 dS m^{-1} (S3) with different levels of humic acid (0.00, 0.25 and 0.50 g L^{-1}), the highest value at 25 day 433.08, 398.10 and 361.51 $mmol^{-l}$ sequentially, while the Magnesium values at 1day were 9.50, 7.20 and 5.62 $mmol^{-1}$ respectively. The release of Magnesium concentrations with water of 7.00 dS m^{-1} (S4) with different levels of humic acid (0.00, 0.25 and 0.50) g L^{-1} was highest in time 25 days (551.11, 418.68 and 387.34) $mmol^{-1}$ in succession. The values of Magnesium released at 1 day are (11.75, 10.00 and 8.50) $mmol^{-1}$ in sequence. It could be conclude from this that the total concentrations of Magnesium from the soil columns were increased with increasing the salinity level of water when not adding the humic acid and decreased with

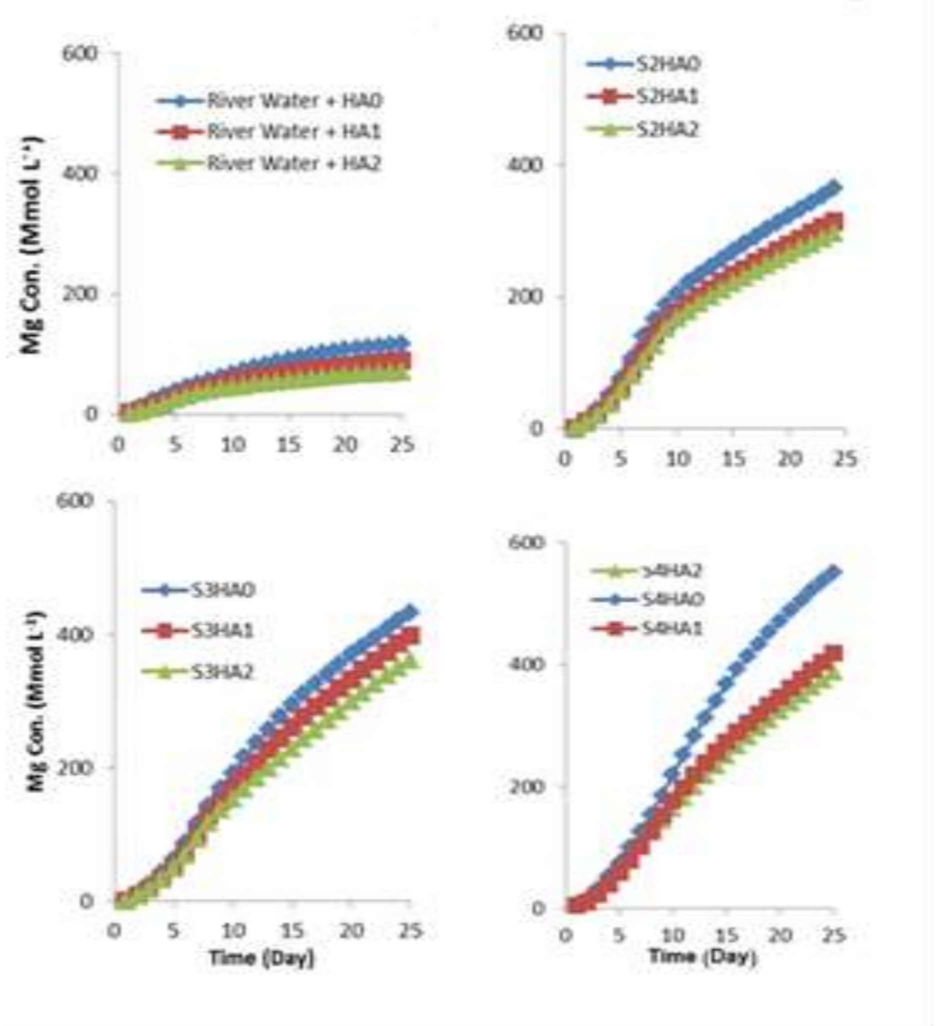

Figure 3. The relationship between Mg^{++} released from water at different salinity levels mixed with different levels of humic acid with time (day).

increasing the levels of added humic acid to all levels of salinity of the water. The amounts of magnesium were reduced to (116.22, 364.29, 433.08and 511 .11) mmol^{-1} with increasing water salinity level (0.72, 3.00, 5.00 and 7.00) dS m^{-1}) in sequence, and when acid is not added to the water. The Magnesium concentrations released were reduced to (88.59, 313.87, 398.10 and 418.68) mmol^{-1} for the same saline water levels respectively, with 0.25 g L^{-1} humic acid. While Magnesium concentrations were reduced to (70.79, 297.50, 361.51, and 387.34) mmol^{-1} when adding the 0.50 g humic acid l^{-1} and the levels of water salinity respectively. The reduction of Magnesium concentrations with increased levels of humic acid is due to the containment of the humic acid on the active groups such as carboxyl and hydroxyl, which acts on the complex and complex of Magnesium ions and the formation of low-mobility organic complexes, which reduces the washing process (23 and 24).

The kinetic of SAR with time

Table 3 showed the mathematical analysis of the five equations used in the experiment, which represented zero order equation, first order equation, second order equation, diffusion equation, and the Elovich equation. The best formula for describing the relationship between the release SAR and time (day) is the diffusion equation, and zero order equation. Although the equation of zero order gave high coefficient of R^2 (0.9713), the diffusion equation gave higher determination coefficient of 0.989, both of which were significant at 0.01. Moreover, the standard error values (SEe) when the diffusion equation gave the value of standard error factor less than the zero order equation at 4.035, the diffusion equation exceeded the remainder of the equations in terms of highest coefficient of measurement and the lowest standard error. The mathematical model $Ct = C0 - Kt^{1/2}$ for diffusion equation is preferable to describe the relationship between SAR released from different salinity levels (0.72, 3.00, 5.00 and 7.00) dS m^{-1} for irrigation water under the influence of various levels of humic acid (0.00 and 0.25 and 0.50) g L^{-1} with time and agree with (1) and (5) who found that the diffusion equation is best in describing the movements of salts. Figure 4 shows the relationship between the released SAR and the time root ($t^{1/2}$). It is observed from the equations that the rate constant reaction (K) increases with increasing the level of added humic acid and any level of salt water used process. The increase in SAR velocity with increasing levels of humic acid is due to the containment of humic acid on the active groups such as carboxyl and hydroxyl which act on the complexity and complexes of Sodium ions and the formation of easy and soluble organic complexes, increasing the speed of washing and increasing SAR (23 and 24). in the experiment. Noting that the rate constant (30.632, 37.003 and 45.253) for the levels of added humic acid of (0.00, 0.25 and 0.50) g l^{-1} in sequence when using the water of 5.0 dS m^{-1} in the washing process.

Table 3. Parameters of different kinetic equations to describe the effect of humic acid in the Sodium adsorption ratio in soil

Treatment	parameters	Zero Order	St . Order 1	2nd Order	Diffusion	Elovich
River water + HA0	R^2	0.987	0.714	0.287	0.991	0.913
	SEe	2.140	0.611	0.230	1.810	5.705
	T	39.294	0.611	-2.765	46.543	14.177
River water + HA1	R^2	0.975	0.774	0.316	0.996	0.870
	SEe	4.496	0.596	0.179	1.786	10.225
	T	69.283	8.073	-3.203	27.239	11.319
River water + HA2	R^2	0.951	0.757	0.296	0.994	0.825
	SEe	8.781	0.842	0.592	3.068	16.666
	T	56.516	7.702	-2.830	19.320	9.482
S2 + HA0	R^2	0.950	0.591	0.170	0.988	0.933
	SEe	6.874	0.855	0.506	3.302	7.970
	T	23.212	6.372	-2.395	49.269	19.840
S2 + HA1	R^2	0.986	0.639	0.164	0.989	0.889
	SEe	4.971	0.859	0.537	4.391	14.431
	T	51.921	7.048	-2.350	45.799	14.975
S2 + HA2	R^2	0.972	0.768	0.278	0.992	0.855
	SEe	8.569	0.603	0.127	4.492	19.749
	T	60.969	9.632	-3.283	31.643	12.876
S3 + HA0	R^2	0.968	0.734	0.193	0.992	0.855
	SEe	6.502	0.730	0.465	3.265	13.997
	T	52.729	7.808	-2.297	26.164	11.422
S3 + HA1	R^2	0.976	0.689	0.176	0.990	0.873
	SEe	6.682	0.808	0.509	4.322	15.620
	T	47.509	6.993	-2.168	30.519	12.348
S3 + HA2	R^2	0.965	0.718	0.181	0.992	0.849
	SEe	10.137	0.801	0.469	4.791	21.241
	T	53.373	7.497	-2.210	24.886	11.139
S4 + HA0	R^2	0.977	0.672	0.182	0.978	0.886
	SEe	6.405	0.892	0.660	6.247	14.363
	T	31.562	6.879	-2.266	32.378	13.404
S4 + HA1	R^2	0.976	0.730	0.221	0.987	0.857
	SEe	8.670	0.779	0.372	5.497	18.559
	T	42.580	7.899	-2.557	26.742	11.752
S4 + HA2	R^2	0.973	0.705	0.186	0.989	0.845
	SEe	10.344	0.905	0.742	5.451	21.394
	T	47.632	7.429	-2.297	24.767	11.215
Rate	R^2	0.9713	0.707	0.220	0.989	0.870
	SEe	7.047	0.773	0.449	4.035	14.993
	T	48.048	6.995	-2.551	32.105	12.829

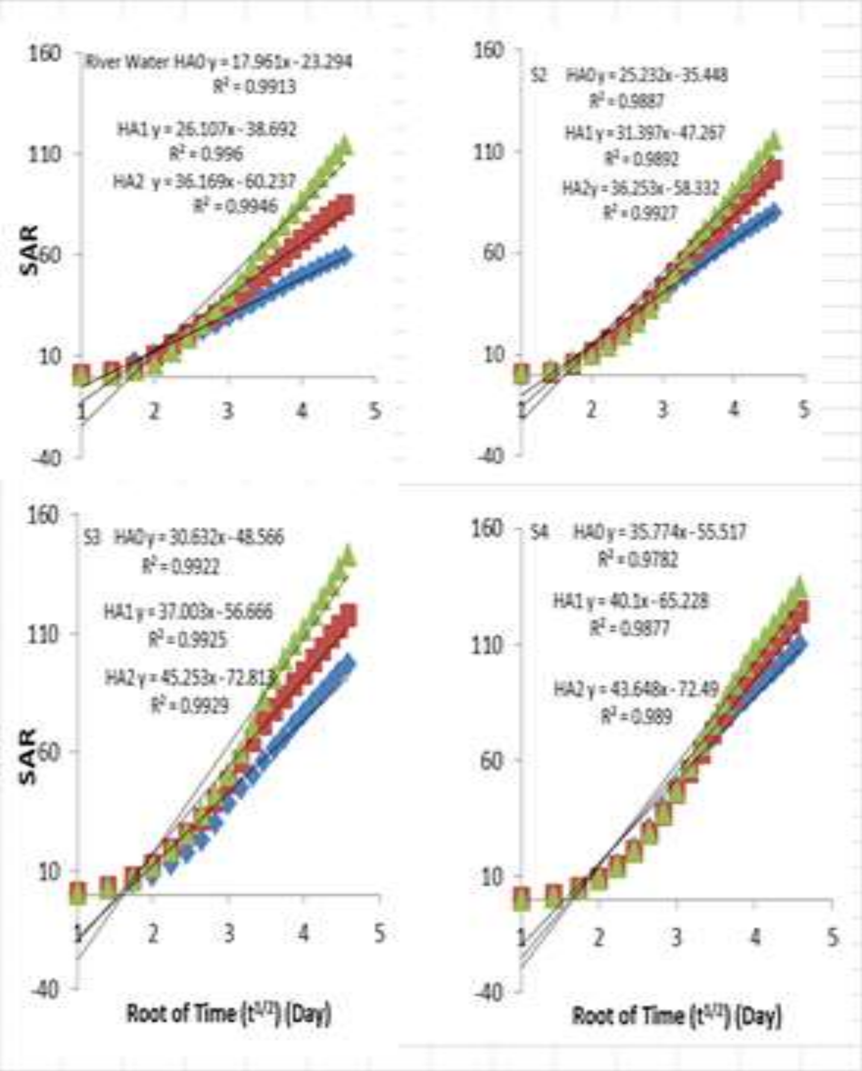

Figure 4. The relationship between SAR resulting from different salinity levels of water blended with levels of humic acid with time (day) according to the diffusion equation

The values of the rate constant reaction (K) increased by (35.774, 40,100 and 43.648) for the levels of added humic acid (0.00, 0.25 and 0.50 g-1) respectively in the use of the water of 7.0 dS m^{-1} in the washing

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