### CALICUM, Mg AND Na RELEASE KINETICS FROM SALINE- SODIC SOIL MIXED WITH SOME AMENDMENTS A. A. Al-Hadethi Z. S. Al-Alwani Prof. Researcher College of Agric- University of Anbar

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#### ABSTRACT

This study was aimed to investigate the effect of phosphogypsum and humic acids on the leaching and releasing of salts from saline- sodic soil. A laboratory experiment was conducted in polyethylene columns (60.0 cm and 7.1 cm). The columns were filled with 30 cm soil (EC=73.78 dSm<sup>-1</sup>). The experiment included two factors, phosphogypsum added at levels 0, 5, 10 and 15 mtons ha<sup>-1</sup> with symbols PG<sub>0</sub>,PG<sub>1</sub>, PG<sub>2</sub> and PG<sub>3</sub> respectively, and humic acids were added at levels 0, 50, 100 and 150 kg ha<sup>-1</sup> with symbols HA<sub>0</sub>, HA<sub>1</sub>, HA<sub>2</sub> and HA<sub>3</sub>, mixing them with the top 5 cm of soil column. The electrical conductivity and the concentrations of water soluble cations (Ca, Mg, and Na) in leachate were determined and sodium adsorption ratio (SAR) was calculated. Results showed that accumulative salts (TDS), sodium released from soil columns increased with increasing the level of addition, whether of phosphogypsum or humic acids. The highest value of salts and sodium released was 682.63 g L<sup>-1</sup> and 7086.12 mmol L<sup>-1</sup> respectively in the treatment PG<sub>3</sub>HA<sub>3</sub>, while the lowest value was 455.94 g L<sup>-1</sup> and 3899.40 mmol L<sup>-1</sup> respectively in the treatment PG<sub>0</sub>HA<sub>0</sub>. Calcium (mmol L<sup>-1</sup>) increased by increasing the level of phosphogypsum, decreased by increasing the level of humic acids, the highest value of accumulated calcium was 1599.0 mmol L<sup>-1</sup> in PG<sub>3</sub>HA<sub>0</sub> while the lowest value was 820.53 mmol  $L^{-1}$  in PG<sub>0</sub>HA<sub>3</sub>. The results showed that the best equation for describing release kinetics of sodium adsorption ratio in soil is the diffusion equation. Increasing level of phosphogypsum and humic acids increased the release constant velocity (K) of sodium adsorption ratio.

Keywords: total dissolved salt, accumulated salts, accumulated Na, accumulated Ca, diffusion Equation.

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المستخلص

لدراسة تأثير الجبس الفوسفاتي والأحماض الدبالية في غسل وتحرر الأملاح من التربة أجريت تجربة مختبرية استخدمت فيها أعمدة من البولي أثلين بارتفاع 60.0 سم وقطر داخلي 7.1 سم، عبئت الأعمدة بالتربة ويعمق 30 سم (ايصاليتها الكهريائية 73.87 ديسسيمنز م-1)، شملت التجربة عاملين، الجبس الفوسفاتي وأضيف بالمستويات 0 و5 و10 و15 طن ه<sup>-1</sup> ورمز لها PG<sub>0</sub> PG وPG وPG وRO والأحماض الدبالية وأضيفت بالمستويات 0 و50 و100 و100 و100 كغم ه<sup>-1</sup> ورمز لها AB وAH وAL وAL ود HA، وذلك بخلطهما مع ال5 سم الأولى من تربة العمود ويمكرر واحد لكل معاملية بعيث أصبح عددها 16 عمود. استخدمت طريقة الغسل المستمر باستخدام ماء بئر ذو ايصالية كهربائية 2.72 دسيسيمنز م<sup>-1</sup>. قدرت الايصالية معاملة بحيث أصبح عددها 16 عمود. استخدمت طريقة الغسل المستمر باستخدام ماء بئر ذو ايصالية كهربائية 2.72 دسيسيمنز م<sup>-1</sup>. قدرت الايصالية مالكربائية وتركيز الأيونات الذائبة الموجبة (Ca A) (Ca A) في الراشح وحسبت نسبة إمتزاز الصوديوم (SAR). أظهرت النتائج أن الأملاح الذائبة الكهربائية وتركيز الأيونات الذائبة الموجبة (Ca A) (Ca A) في الراشح وحسبت نسبة إمتزاز الصوديوم (SAR). أظهرت النتائج أن الأملاح الذائبة الكهربائية وتركيز الأيونات الذائبة الموجبة (Ca A) (Ca A) في الراشح وحسبت نسبة إمتزاز الصوديوم (SAR). أظهرت النتائج أن الأملاح الذائبة الكهربائية وتركيز الأيونات الذائبة الموجبة (Ca A) التجميعية المتحررة من أعمدة التربة ازدادت بزيادة مستوى الإضافة سواء من الجبس الفوسفاتي أو المحماض الدبالية أو التداخل بينهما، إذ بنغت أعلى قيمة للأملاح والصوديوم المتحرر 68.20 عملا و 2.10 بالتتابع في المعاملة دوAB منه معاملة وPG<sub>0</sub>AA من التر<sup>-1</sup> وAB وAD والصوديوم المتحرر قد 68.20 عملتر<sup>-1</sup> و 20.60 مليمول لتر<sup>-1</sup> بالتتابع في المعاملة دوAB المعاملة مو 100 من الذبلين أقل قيمة للأملاح والصوديوم المتحرر في المتوبي في المعاملة معام 10 معملة المعاملة وPG<sub>3</sub>HA منهما إذ بنغت أقل قيمة 455.94 عم لتر<sup>-1</sup> و 20.40 والصوديوم لير<sup>-1</sup> بالتتابع في المعاملة مو 40.40 والمود التر<sup>-1</sup>) التجميعي المتحرر بزيادة مستوى الإضافة من الجبس الفوسفاتي، وانخفض بزيادة مستوى الإضاف الداليوال الدالي الدمان الدالية، والمعاملة مو 40.40 والمود المعاملة وPG<sub>1</sub> مرار<sup>-1</sup> التجميعي مليمول لتر<sup>-1</sup> في المعاملة وPG<sub>3</sub>HA في حين بلغت أقل قيمة 20.53 مليمو

كلمات مفتاحية: الاملاح الذائبة الكلية، الاملاح التجميعية، الصوديوم التجميعي، الكالسيوم التجميعي، معادلة الانتشار،

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### INTRODUCTION

Soil salinity is one of the major problems hindering agriculture. The area of land affected by salts is estimated at 7% of the world's land and more than 50% of agricultural land (16). The time and efficiency of removing salts from the soil by leaching depends on the quality of salts present in the soil, because of the solubility of salts and the nature of their constituent ions, as well as the variation of the cations constituents of the salts on adsorption and exchange on soil surfaces. Removing salts from the soil by leaching is not a simple process, during the movement of soluble salts with leachate, ion exchange occurs between soil colloids and the solution passing through them. Shainberg and Letey (24) pointed to the danger of removal of salts from the saline sodic soils because the velocity of removal of soluble salts is greater than the velocity of the removal of exchange sodium, which is why the soil turned into sodic during leaching. It is therefore necessary to find means to manage the soil and not to deteriorate its chemical and physical properties. One of these methods is to use chemical and organic amendments to synchronize with the leaching process (5). Phosphogypsum is one of the most important chemical amendments; it is a calcium sulphate (CaSO<sub>4</sub>.2H<sub>2</sub>O), which is produced by the phosphate fertilizer industry (25). Phosphogypsum is added as an amendments in the reclamation of the saline sodic soils, which is characterized by the dominant of sodium ion on the exchange complex, for the purpose of providing calcium ion (14, 23, and 24), it can be used to reduce sodium adsorption ratio in both soil and irrigation water. It was found that the addition of phosphogypsum at the level of 7.5 and 15.0 mtons ha<sup>-1</sup> resulted in a significant decrease in the sodium exchange values (3). Al-Muhamdi (10) obtained the low values of sodium adsorption ratio and increases the values of the electrical conductivity and the concentration of dissolved calcium in the soil by adding phosphogypsum. It was also found that the addition of phosphogypsum to saline - sodic soil resulted in a significant decrease in the values of sodium adsorption ratio, percentage of sodium exchange and increased of calcium in soil (17). Humic acids (humic acid and folvic acid) are organic amendments of saline soils. The addition of humic acids to the soil helps to remove salts and reduce the electrical conductivity and sodium adsorption ratio and regulate the pH. This is can be due to the effectiveness of humic acids in the formation of compounds which works to form complexes with salt ions and make them easy to leached. it is possible to increase the efficiency of the reclamation of salts affected soil. The addition of humic acids led to reduced electrical conductivity and the proportion of sodium adsorption ratio in the soil (22). It was found that the addition of humic acids at levels 24, 36 and 48 kg ha<sup>-1</sup> mixed with soil resulted in a significant decrease in the values of both electrical conductivity and pH (15). It was found that the addition of humic acid caused significant decreases in the values of the electrical conductivity and the percentage of adsorption, and sodium increase the concentration of calcium, in the soil compared to the treatment of non-addition (8). This study investigate the effect aimed to of phosphogypsum and humic acids on the leaching and releasing of salts from calcareous soil (saline - sodic).

#### MATERIALS AND METHODS

A laboratory experiment was carried out to study the effect of phosphogypsum and humic acids on the leaching and release of salts and some dissolved cations in calcareous soils (saline - sodic). Columns of polyethylene were used in 60.0 cm high and 7.1 cm in diameter perforated plastic disk Install bottom at each column, put the glass wool over the disc with a layer of fine gravel of 5 cm. The columns were filled with soil from the surface layer 0-30 cm. Table 1 shows some chemical and physical properties of the soil used. After the soil was air-dried and sieved with a 2 mm diameter sieve. The height of the soil was 30 cm and the weight of 1484 g within the columns and a homogeneous bulk density of 1.25 Mg m<sup>-3</sup>. Four levels of phosphogypsum are 0, 5, 10 and 15 mtons ha<sup>-1</sup>, equivalent to 0, 2, 4 and 6 g kg<sup>-1</sup> with symbols PG<sub>0</sub>,PG<sub>1</sub>, PG<sub>2</sub> and PG<sub>3</sub>, and four levels of humic acids are 0, 50, 100 and 150 kg  $ha^{-1}$ , equivalent to 0.00, 0.02 and 0.04 and 0.06 g kg<sup>-1</sup> with symbols HA<sub>0</sub>, HA<sub>1</sub>, HA<sub>2</sub> and HA<sub>3</sub>, mixed with the first 5 cm of soil treatment so that the total columns became 16 columns. All the columns moistened by means of the capillary property to maintain homogeneity of moisture content throughout the column. The continuous leaching method was used with well water of an electrical conductivity 2.72 dSm<sup>-1</sup> and table 2 showing some chemical properties of water used for leaching. A fixed water column of 15 cm high above the surface of the soil were done using the technique of communicating vessels. The leachate was collected daily for each column individually. The leaching process continued until the electrical conductivity of the filtration reached 3-5 dS m<sup>-1</sup>. Electrical conductivity and concentration of dissolved cations (Ca, Mg, and Na) were determined. The following were calculated:

1- The amount of total dissolved salts (TDS)  $(g L^{-1})$  in the leaching water using the following equation:

$$g.L^{-1} = EC \times 0.640$$

2- The sodium adsorption ratio (SAR) in the leaching water using the following equation:

$$SAR = \frac{Na}{\sqrt{Ca + Mg}}$$

\*Concentrations of Na, Ca and Mg were calculated in (mmol  $L^{-1}$ ).

Results were subjected to kinetic equations to study the release of sodium adsorption ratio with time.

#### The kinetic equations used in the study:

Mathematical equations based on kinetic chemistry were used, to study the release kinetics of salts and sodium adsorption ratio in leachate with time, referred to by (27). These equations are:

1- Zero order eq.	$C_t = C_0 - Kt$
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3- Second order eq.  $1/C_t = 1/C_0 + Kt$ 

 $C_t = C_0 - Kt^{1/2}$ 4- diffusion eq.  $C_t = C_0 - K \ln t$ 

5- Elovich eq.

**Representing:** 

 $C_0 = SAR$  in leachate at zero time

 $C_t = SAR$  in the leachate at the specified time

K = release rate constant of SAR

To determine the most efficient equation to describe the release of SAR, the following indicators were adopted: Determination Coefficient  $(R^2)$ , Stander Error of Estimate (SEe), T= table value (variance between values).

#### Table 1. Some chemical and physical properties of soil

Bulk	4	CEC	ом	C-CO	CO CaSO <sub>4</sub> . ESP SAP dissolved cations		<b>S</b>		ECa				
density		SAR	к К <sup>+</sup>	$\mathbf{Mg}^{++}$	Ca <sup>++</sup>	$Na^+$	рН	ECe					
Mg m <sup>-3</sup>	Silty	Cmol kg <sup>-1-</sup> soil		g kg <sup>-1</sup> % mmol L <sup>-1</sup>							dS m <sup>-1</sup>		
1.25	loam	24.65	3.52	249.00	56.78	36.41	39.68	3.46	25.00	110.25	461.50	7.72	73.78
Table 2. Some chemical properties of well water used in the experiment													

Property	EC	pН		dissolved	SAR	Water		
			$Na^+$	<b>Ca</b> <sup>++</sup>	$Mg^{++}$	$\mathbf{K}^{+}$		class
value	2.72	7.44	4.42	6.48	4.97	0.23	1.31	
unite	dS m <sup>-1</sup>	-		mmo	-	$C_4S_1$		

#### Table 3. Some chemical properties of Phosphogypsum used in the experiment

Property	EC	pН	po	sitive di	ssolved io	CaCO <sub>3</sub>	CaSO <sub>4</sub> .	
	1:1	1:1	$Na^+$	<b>Ca</b> <sup>++</sup>	$Mg^{++}$	$\mathbf{K}^+$		2H <sub>2</sub> O
value	4.03	5.76	4.42	6.48	4.97	0.23	121.36	856.90
unite	dS m <sup>-1</sup>	-		mmol I <sup>-1</sup>			g Kg <sup>-1</sup>	

#### **RESULTS AND DISCUSSION** Salts released (g L<sup>-1</sup>) with pore volume

Figure 1 show the relationship between the amounts of salts accumulated (g  $L^{-1}$ ) released from soil columns with pore volume under the influence of phosphogypsum and humic acids. It is observe that the amount of salts released

increased by increasing the pore volume (leachate passing through the soil columns) this is true for all treatments as well as the noaddiction treatment. This is consistent with findings of other researchers (2, 6, 7, 17, 18, and 19) who indicated that the amount of salts accumulated released increased by increasing

the amount of leaching water passing through the soil column. It is also observed that the amount of salts released under the influence of phosphogypsum increased by increasing the level of addition of PG1HA0, PG2HA0 and PG<sub>3</sub>HA<sub>0</sub> compared to the treatment of nonaddition PG<sub>0</sub>HA<sub>0</sub>, the amount of released salts at pore volume 3 reached 506.36, 577.35 and  $669.84 \text{ g L}^{-1}$  respectively, with an increase of 11.06%, 26.63% and 46.91% sequentially in relation to the non-additive treatment, which reached 455.94 g  $L^{-1}$ . The increase in the amount of salts released by the addition of phosphogypsum is due to its role in increasing the concentration of calcium and sulfate in the solution during its solubility, soil thus

increasing the electrolytic concentration, and then move down with washed leachate (7 and 19), in addition to the role of phosphogypsum in reducing the bulk density and improve the structure of soil and water conductivity and increase the rate of infiltration which reflected positively in increasing the rate of leaching salts (3 and 10). These results are consistent with the findings (6, 15, 16, and 17) who pointed out that the amount of salts released from soil columns increased with the addition of phosphogypsum. It is also observe that the above increase in the amount of salts released by increasing the level of addition of phosphogypsum is true at all levels of humic acids.

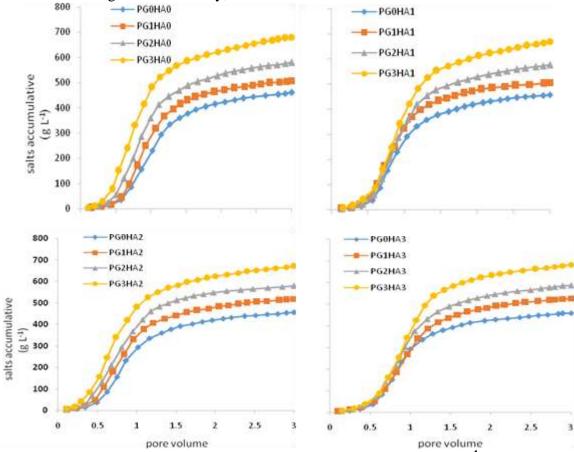


Figure 1. The relationship between the amounts of accumulated salts (g L<sup>-1</sup>) released from soil columns with the pore volume under the influence of phosphogypsum and humic acids

It is also observed that the amount of salts released under the influence of humic acids increased by increasing the level of addition  $PG_0HA_1$ ,  $PG_0HA_2$  and  $PG_0HA_3$  compared to the treatment of non-addition  $PG_0HA_0$ , the amount of released salts at pore volume 3 reached 458.59, 460.57 and 461.63 g L<sup>-1</sup>, with an increase of 0.58%, 1.01% and 1.24% respectively compared to the non-additive treatment, which reached 455.94 g L<sup>-1</sup>. The

increase in the amount of released salts by adding humic acids can be due to its role in improving soil chemical properties by containing the active groups such as carboxyl and hydroxyl groups which work on the chelating, complexity and adsorption of saline elements, changing the ionic structure of the soil solution, by leaching the sodium salts out of the soil section, thereby reducing their effect on the soil (28), in addition to the ability of humic acids to improve the soil physical properties of soil (21 and 29). These results are consistent with the findings (1, 6, and 15). It is also observed that the above increase in the amount of released salts by increasing the level of addition of humic acids is true at all levels of phosphogypsum. The effect of the interaction between phosphogypsum and humic acids in the amount of released salts from soil columns, it is observe that the amount of released salts from any level of phosphogypsum  $PG_0$ ,  $PG_1$ ,  $PG_2$  and  $PG_3$ increased by increasing the level of addition of humic acids HA<sub>0</sub>, HA<sub>1</sub>, HA<sub>2</sub> and HA<sub>3</sub>, the treatment gave PG<sub>3</sub>HA<sub>3</sub> the highest value of released salts at pore volume 3 reached 682.63  $L^{-1}$  with an increase reached 49.72% g compared to the treatment of non-addition  $PG_0HA_0$  with 455.94 g L<sup>-1</sup>.

## Calcium released (mmol L<sup>-1</sup>) with pore volume

Figure 2 shows the relationship between the concentrations of accumulated calcium (mmol  $L^{-1}$ ) released from soil columns with pore volume under the influence of phosphogypsum and humic acids. It can be shown that concentration of the accumulated calcium released increased by increasing the pore volume this is true for all treatments as well as the non-addition treatment. This is consistent with the findings of other researcher (6, 7, 12, 17, and 19) who pointed out that the concentration of calcium released increased the amount of leaching water passing through the soil column. It can be shown that the concentration of calcium released under the effect of phosphogypsum increased by increasing the level of addition of PG<sub>1</sub>HA<sub>0</sub>,  $PG_2HA_0$  and  $PG_3HA_0$  compared to the treatment of non-addition PG<sub>0</sub>HA<sub>0</sub>, calcium concentration accumulated released at pore volume 3 reached 1212.7, 1323.4 and 1599.0 mmol  $L^{-1}$  respectively, with an increase of 8.19%, 18.07% and 42.65% in relation to the non-addition treatment. which had a concentration of accumulated calcium released 1120.9 mmol  $L^{-1}$ . The increase in the amount of calcium released by adding phosphogypsum was due to its role in increasing the concentration of calcium ions in the soil solution during its solubility

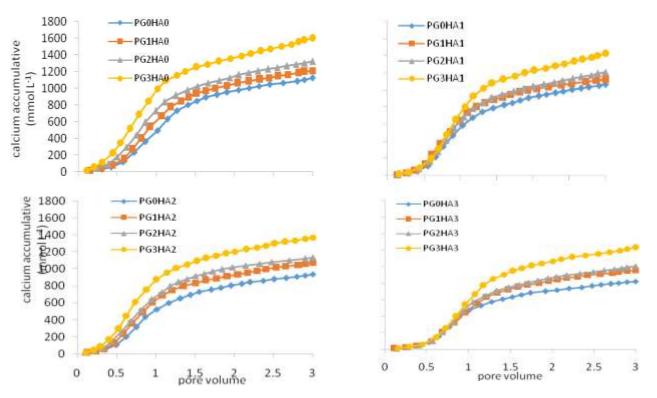
(3 and 10). These results are consistent with the findings of other researchers (6 and 17) who pointed out that the addition of phosphogypsum has increased the concentration of calcium released from soil columns. It is also observed that the above increase in calcium concentration by phosphogypsum was due to its role in increasing the concentration of calcium ions in the soil solution during its solubility (3 and 11), in addition to the role of phosphogypsum in reducing the bulk density and improve soil physical properties and water movement the level of addition increasing of phosphogypsum is true at all levels of humic acids. It can be observed that the concentration of calcium released under the effect of humic acids decreased by increasing the level of addition PG<sub>0</sub>HA<sub>1</sub> and PG<sub>0</sub>HA<sub>2</sub> and PG<sub>0</sub>HA<sub>3</sub> compared to the treatment of non-addition PG<sub>0</sub>HA<sub>0</sub>, calcium concentration accumulated released at pore volume 3 reached 1064.92, 935.82 and 820.53 mmol  $L^{-1}$  respectively, with a decrease of 4.99%, 16.51% and 26.79% respectively compared to the non-addiction treatment, which had a concentration of calcium accumulated released 1120.9 mmol L<sup>-</sup> <sup>1</sup>. The decrease in the concentration of released calcium by the addition of humic acids is attributed to the presence of active groups such as carboxylic and hydroxyl groups that act on the complexity and chelating of calcium ions and the formation of organic complexes that are less volatile in the soil than the magnesium, potassium and sodium ions, which reduces the leaching process (8 and 28) these results are consistent with the findings (5) which indicated that the concentration of calcium released from soil columns decreased by increasing the level of addition of humic acid. It is also observed that the above reduction in calcium concentration bv increasing the level of addition of humic acids is correct at all levels of addition of phosphogypsum. The effect of the interaction between phosphogypsum and humic acids in the concentration of calcium released from soil columns, it is observe that the concentration of calcium accumulated released from any addition level of phosphogypsum PG<sub>0</sub>, PG<sub>1</sub>, PG<sub>2</sub> and PG<sub>3</sub> decreased by increasing the level of addition of humic acids HA<sub>0</sub>, HA<sub>1</sub>, HA<sub>2</sub> and

48.68% compared to PG<sub>3</sub>HA<sub>0</sub>, which gave the

highest value concentration of calcium

accumulated released reached 1599.0 mmol

HA<sub>3</sub>, the treatment gave  $PG_0HA_3$  the lowest value of the concentration of calcium accumulated released at pore volume 3 reached 820.53 mmol L<sup>-1</sup> and a decrease of



 $L^{-1}$ .

Figure 2. The relationship between the amounts of accumulated calcium (mmol L<sup>-1</sup>) released from soil columns with the pore volume under the influence of phosphogypsum and humic

acids volume 3 reached 4351.0, 5025.1 and 5698.3

## Sodium released (mmol L<sup>-1</sup>) with pore volume

Figure 3 shows the relationship between the concentrations of accumulated sodium (mmol  $L^{-1}$ ) released from soil columns with pore volume under the influence of phosphogypsum humic acids. It is observe and that concentration of the sodium accumulated released increased by increasing the pore volume (leachate passing through the soil columns) this is true for all treatments as well the non-addition treatment. This is as with the findings of other consistent researchers (6, 7, 18, and 19) who pointed out that the concentration of sodium removed from the soil columns increased by increasing the amount of leaching water passing through the soil column. It can be also observed that the concentration of sodium released under the effect of phosphogypsum increased by increasing the level of addition of PG<sub>1</sub>HA<sub>0</sub>,  $PG_2HA_0$  and  $PG_3HA_0$  compared to the treatment of non-addition  $PG_0HA_0$ , the concentration of sodium released at pore

mmol  $L^{-1}$  respectively, with an increase of 11.58%, 28.86% and 46.13% respectively in compared to the non-addition treatment, which the concentration of sodium released reached 3899.4 mmol  $L^{-1}$ . The increase in the concentration of sodium released by the addition of phosphogypsum was due to its role in increasing the concentration of calcium ions in the soil solution during its solubility, replacing the sodium ions on the exchange sites and displacing the latter outside the soil section with leaching water (3 and 30), in addition to the role of phosphogypsum in reducing the bulk density of soil and improve the structure and water conductivity and increase the rate of infiltration, which is reflected positively in increasing the rate of displacement of salts (3 and 11) these results are consistent with the findings of other researchers (7, 17, 18, and 19) who pointed out that the addition of phosphogypsum led to an increase in the rate of displacement of sodium from the soil. It is also observed that the

concentration of sodium released under the effect of humic acids increased by increasing the level of HA addition PG0HA1, PG0HA2 and PG0HA3 compared to the treatment of non-addition PG0HA0, the concentration of sodium released at pore volume 3 reached 4139.03, 4430.23 and 4871.43 mmol L<sup>-1</sup> respectively, with an increase of 6.15%, 13.61% and 24.93% respectively, which the concentration of sodium accumulated released

was 3899.40 mmol  $L^{-1}$ . The increased concentration of sodium released by the addition of humic acids is due to the presence of active groups such as carboxyl and hydroxyl groups that act on the chelating, complexity and adsorption of sodium ions, formation of easily soluble organic complexes and faster soil movement of calcium, magnesium and

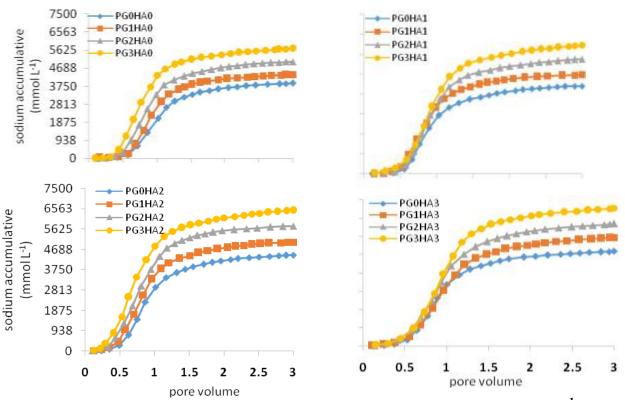


Figure 3. The relationship between the amounts of accumulated sodium (mmol L<sup>-1</sup>) released from soil columns with the pore volume under the influence of phosphogypsum and humic acids

#### The kinetic of SAR with time (day)

Several mathematical equations based on the basis of chemical kinetic were used to describe the relationship between of the sodium adsorption ratio accumulation released from soil columns with time (day) under the influence of phosphogypsum and humic acids, data on sodium adsorption ratio were subjected to kinetic equations, the results in Table 4 show the mathematical analysis of the five kinetic equations (Zero order eq, 1<sup>st</sup> order eq,  $2^{nd}$  order eq, Diffusion eq and Elovich eq) used in the laboratory experiment. The results showed that the best equation for describing the relationship between of the sodium adsorption ratio released and time (day) is Diffusion equation. Although the Elovich equation gave a high  $R^2$  reached 0.922, the Diffusion equation gave a higher  $R^2$  than Elovich equation reached 0.958, both of which were significant at 0.01, while the standard error values for the Elovich equation were high at 50.330 while Diffusion equation gave the value of the standard error less than the Elovich equation at 36.375. This means that Diffusion equation exceeded the other equations in terms of the highest average of the  $R^2$  and the lowest standard estimation error (SEe). The mathematical model of Diffusion equation  $C_t = C_0 - Kt^{1/2}$  it is best to describe the relationship between sodium adsorption ratio released from soil columns with time (day) under the influence of phosphogypsum and humic acids. These results are similar to

those of the other researchers (4, 8, 12, and 13)who found that Diffusion equation is best to describe the sodium adsorption ratio. Figure 4 shows the relationship between the sodium adsorption ratio released from soil columns with the root of time  $(t^{1/2})$  (day) under the influence of phosphogypsum and humic acids, the linear equations show that of the release rate constant (K) of the sodium adsorption ratio increased by increasing the addition level of phosphogypsum, the release rate constant reached 117.23, 125.47, 139.79 and 144.21 for PG<sub>0</sub>HA<sub>0</sub>, PG<sub>1</sub>HA<sub>0</sub>, PG<sub>2</sub>HA<sub>0</sub> and PG<sub>3</sub>HA<sub>0</sub> respectively. The increase in the release rate constant of sodium adsorption ratio by the addition of phosphogypsum was attributed to its role in increasing the concentration of calcium and magnesium ions in the soil solution during its solubility, replacing sodium ions on the exchange sites and displacing the latter outside the soil section with leaching water (3 and 30) which increases the concentration of sodium in the leaching water thus increasing the sodium adsorption ratio released from the soil, in addition to the role of phosphogypsum in reducing the bulk density and improve soil structure and water conductivity and increase the rate of infiltration, which is reflected positively in increasing the rate of leaching salt ions (3 and 11). It is observed that the above-mentioned increase in the release rate constant of the sodium adsorption ratio by increasing the level of addition of phosphogypsum is true at all levels of humic acids. The linear equations also show that the release rate constant (K) of the sodium adsorption ratio increased by increasing the level of addition of humic acids, the release rate constant reached 117.23, 132.03, 150.33 and 179.39 for PG<sub>0</sub>HA<sub>0</sub>, PG<sub>0</sub>HA<sub>1</sub>, PG<sub>0</sub>HA<sub>2</sub> and PG<sub>0</sub>HA<sub>3</sub> respectively. The increase in the release of sodium adsorption ratio by the addition of humic acids is attributed to the presence of active groups such as carboxyl and hydroxyl groups that act on the chelating, complexity and adsorption of sodium ions, and the formation of organic compounds easily soluble and movement, thus increasing the leaching process. The active groups in humic acids also work on the calcium and magnesium ion chelating and complexes and the formation of organic compounds that are less movement in the soil than sodium ion, thus reducing their leaching process (9 and 31) therefore, the concentration of sodium is increased relative to the concentration of calcium and magnesium in the leaching water, which causes an increase in sodium adsorption ratio. These results are consistent with (8), which found that the release velocity of sodium adsorption ratio increased with the addition of humic acid. It is observed that the above-mentioned increase in the release velocity of sodium adsorption ratio by increasing the level of addition of humic acids is true at all levels of phosphogypsum. Effect Interaction between of the Phosphogypsum and Humic Acids in constant of the release velocity (K), it is observed from the linear equations that constant of the release velocity (K) at any level of phosphogypsum  $PG_0$ ,  $PG_1$ ,  $PG_2$  and

# Table 4. Parameters of difference kinetic equations to describe the effect of phosphogypsum and humic acids in the movement of sodium adsorption ratio in soil columns

treatment	Indicators	Zero - Order	1 <sup>st</sup> order	2 <sup>nd</sup> order	Diffusion	Elovich
	$\mathbf{R}^2$	0.907	0.634	0.235	0.952	0.909
PG <sub>0</sub> HA <sub>0</sub>	SE <sub>e</sub>	40.230	1.050	0.217	28.930	39.803
	Ť	14.010	5.897	-2.482	19.291	14.176
	$\mathbf{R}^2$	0.902	0.645	0.270	0.948	0.908
PG <sub>1</sub> HA <sub>0</sub>	SEe	44.376	0.981	0.130	32.052	42.866
-1 0	T	13.577	6.039	-2.721	19.279	14.106
	$\mathbf{R}^2$	0.904	0.650	0.293	0.952	0.913
PG <sub>2</sub> HA <sub>0</sub>	SEe	48.773	0.924	0.084	34.495	46.463
20	T	13.757	6.094	-2.885	19.958	14.512
	$\mathbf{R}^2$	0.898	0.637	0.286	0.949	0.915
PG <sub>3</sub> HA <sub>0</sub>	SE <sub>e</sub>	52.023	0.955	0.089	36.450	47.263
1 031110	БЕ <sub>е</sub> Т	13.274	5.925	-2.832	19.485	14.751
	$\mathbf{R}^2$	0.913	0.644	0.267	0.956	0.911
PG <sub>0</sub> HA <sub>1</sub>	SE <sub>e</sub>	43.758	0.987	0.131	31.047	44.124
1 <b>G</b> <sub>0</sub> 11A <sub>1</sub>	ы Т	14.522	6.017	-2.701	20.944	14.39
	$\mathbf{R}^2$	0.912	0.641	0.271	0.957	0.916
		47.995	0.938	0.094	33.262	46.788
PG <sub>1</sub> HA <sub>1</sub>	SE <sub>e</sub>	14.432	5.987	-2.729	21.338	14.84
	T R <sup>2</sup>	0.906	0.643	0.283	0.954	0.915
		54.563	0.939	0.285		
PG <sub>2</sub> HA <sub>1</sub>	SE <sub>e</sub>				38.173	51.897 14 705
	$\mathbf{T}$ $\mathbf{p}^{2}$	13.919	6.007	-2.810	20.412	14.705
	$\mathbf{R}^2$	0.908	0.679	0.306	0.961	0.927
PG <sub>3</sub> HA <sub>1</sub>	SEe	54.027	0.674	0.024	35.535	48.054
	T	14.124	6.510	-2.973	22.077	16.045
	$\mathbb{R}^2$	0.911	0.653	0.281	0.954	0.91
PG <sub>0</sub> HA <sub>2</sub>	SE <sub>e</sub>	50.428	0.930	0.088	36.044	50.713
	Т	14.345	6.144	-2.802	20.540	14.256
	$\mathbf{R}^2$	0.915	0.668	0.281	0.961	0.919
PG <sub>1</sub> HA <sub>2</sub>	SE <sub>e</sub>	52.244	0.784	0.044	35.587	51.104
	Т	14.767	6.355	-2.802	22.206	15.126
	$\mathbb{R}^2$	0.908	0.650	0.270	0.959	0.962
PG <sub>2</sub> HA <sub>2</sub>	SEe	60.031	0.804	0.042	39.866	53.873
	T	14.055	6.094	-2.720	21.756	15.816
	$\mathbf{R}^2$	0.910	0.670	0.307	0.965	0.937
PG <sub>3</sub> HA <sub>2</sub>	SE <sub>e</sub>	59.464	0.656	0.019	36.997	49.739
	Т	14.288	6.373	-2.981	23.644	17.331
	$\mathbf{R}^2$	0.915	0.652	0.252	0.958	0.912
PG <sub>0</sub> HA <sub>3</sub>	SEe	58.504	0.903	0.075	41.265	59.593
	Т	14.765	6.134	-2.597	21.411	14.47
	$\mathbf{R}^2$	0.923	0.663	0.246	0.966	0.924
PG <sub>1</sub> HA <sub>3</sub>	SE <sub>e</sub>	58.999	0.765	0.039	38.822	58.492
	Т	15.513	6.272	-2.559	24.125	15.658
	$\mathbf{R}^2$	0.916	0.646	0.243	0.968	0.937
PG <sub>2</sub> HA <sub>3</sub>	SE <sub>e</sub>	66.474	0.729	0.028	40.964	57.633
	Т	14.788	6.054	-2.533	24.668	17.249
	$\mathbf{R}^2$	0.910	0.659	0.289	0.966	0.939
PG <sub>3</sub> HA <sub>3</sub>	SEe	69.033	0.675	0.018	42.508	56.879
	Т	14.275	6.227	-2.853	23.878	17.591
	$\mathbf{R}^2$	0.910	0.652	0.274	0.958	0.922
Average	SEe	53.808	0.856	0.075	36.375	50.330
_	T	14.276	6.133	-2.749	21.563	15.314

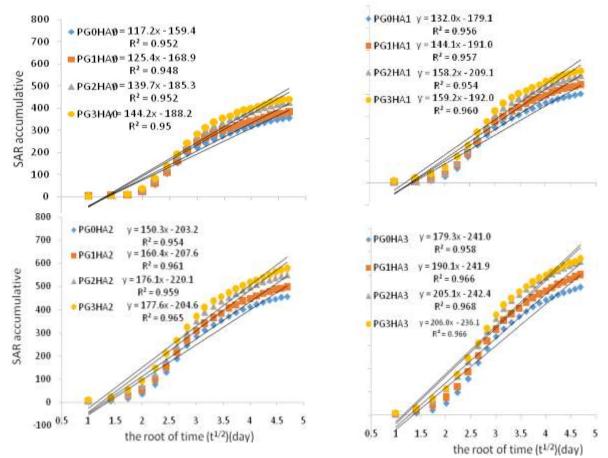


Figure 4. The relationship between the accumulation released of SAR with the root of time  $(t^{1/2})$  (day) under the effect of phosphogypsum and humic acids according to the Parabolic diffusion equation

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