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Effect of Irrigation Water Quality and Wetting and Drying Cycles on the Release of Calcium and Magnesium from Two Soils with Different Textures

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ABSTRACT

KEY WORDS:

Irrigation water, Gapon constant, kinetic equations , wetting and drying cycles.

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The study included two sites for two soils with different textures (Al-Mazara and Bashiqa) within Nineveh Governorate - Iraq. Soil samples were taken from the surface depth (30 cm) naturally by means of columns. The experiment was carried out by adding two types of water (river water and well water) to each column with a volume equivalent to The pore size, and alternating wetting and drying were done for ten cycles, and the period between one cycle and another was 10 days. Soil samples were analyzed after the first cycle, the fifth cycle, and the tenth cycle to find out the effect of the number of wetting cycles on the exchanged ions, the relative effectiveness, and the Gapon constant. The results indicated that the released amount of exchanged calcium ions in the soil of Bashiqa was higher than the amount released in the soil of the Al-Mazara, while the amount of magnesium ions released in the soil of Al-Mazara was higher than the amount released in the soil of Bashiqa and when using both types of water, while the relative effectiveness values for calcium, the values were higher when wetting with well water, except for the first cycle in the soil of Al-Mazara and the tenth cycle in the soil of Al-Mazara and Bashiqa, while the relative effectiveness of magnesium in the two study soils, the values were higher when wetting with well water and for all cycles except the fifth cycle in Bashiqa soil, while the Gapon constant for calcium in the two study soils had higher values when wetting with river water in the fifth cycles, while in the first and tenth cycles the values were higher when wetting with well water, except for the first cycle in Bashiqa soil, while the Gapon constant for magnesium in the two study soils, the values were higher when wetting with well water and for all cycles except for the first and fifth cycle in Al-Mazara soil. Then the following kinetic equations were applied: zero order equation, first order equation, diffusion equation, Elovich equation and power function equation, the power function equation was the best equation that describes the process of release calcium and magnesium ions in the study soil.

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تأثير نوعية مياه الري ودورات الترطيب والتجفيف على تحرر الكالسيوم والمغنسيوم من تربتين مختلفتي النسجة

ريم اياد عبدالحليم القطان و قحطان درويش عيسى الخفاجي قسم علوم التربة والموارد المائية / كلية الزراعة والغابات / جامعة الموصل

الخالصة

شملت الدراسة موقعين لتربيتن مختلفتين في النسجة (حي المزارع وبعشيقة) ضمن محافظة نينوى – العراق, اخذت عينات التربة من العمق السطحي (30 سم) بشكل طبيعي بواسطة أعمدة, نفذت التجربة باضافة نوعين من المياه (ماء نهر وماء بئر) الى كل عمود بحجم يعادل الحجم المسامي, وتم عمل ترطيب وتجفيف متناوب لعشرة دورات والفترة بين دورة وأخرى 10 ايام, تم تحليل عينات التربة بعد الدورة االولى والدورة الخامسة والدورة العاشرة لمعرفة تأثير عدد دورات الترطيب على االيونات المتبادلة والفعالية النسبية وثابت كابون, اشارت النتائج بأن الكمية المتحررة من ايونات الكالسيوم المتبادلة في تربة بعشيقة كانت أعلى من كميتها المتحررة في تربة حي المزارع, أما الكمية المتحررة من أيونات المغنسيوم في تربة حي المزارع كانت أعلى من كميتها المتحررة في تربة بعشيقة وعند استخدام المياه بنوعيها, بينما قيم الفعالية النسبية للكالسيوم كانت القيم اعلى عند الترطيب بمياه البئر باستثناء الدورة االولى في تربة حي المزارع والدورة العاشرة في تربتي حي المزارع وبعشيقة, في حين الفعالية النسبية للمغنسيوم في تربتي الدراسة كانت القيم اعلى عند الترطيب بمياه البئر ولجميع الدورات باستثناء الدورة الخامسة في تربة بعشيقة, أما ثابت كابون للكالسيوم في تربتي الدراسة كانت قيمه اعلى عند الترطيب بمياه النهر في الدورة الخامسة, اما في الدورة االولى والعاشرة كانت القيم اعلى عند الترطيب بمياه البئر باستثناء الدورة االولى في تربة بعشيقة, في حين ثابت كابون للمغنسيوم في تربتي الدراسة كانت القيم اعلى عند الترطيب بمياه البئر ولجميع الدورات باستثناء الدورة االولى والخامسة في تربة حي المزارع. ثم طبقت المعادلات الحركية التالية (Parabolic diffusion ,First order equation ,Zero order equation equation, equation Elovich و equation Function – Power)فكانت معادلة دالة القوة افضل معادلة تصف عملية تحرر ايونات الكالسيوم والمغنسيوم في ترب الدراسة.

الكلمات المفتاحية: ماء الري , ثابت كابون , المعادالت الحركية , دورات الترطيب والتجفيف.

INTRODUCTION

Irrigation water contains varying amounts of dissolved ions, and the amount of these ions in the irrigation water affects the quality of the ions that prevail in the soil solution, meaning that the use of water with a high concentration of a certain ion leads to the dominance of that ion on the exchange surfaces, and this affects the readiness and absorption of ions other (Al-Hadidi *et al*., 2007). Also, the quality of the irrigation water has a direct effect on the composition of the soil solution, and the soil irrigation process results in the desorption or precipitation of ions in the soil, and this is related to the different soil properties, and when the irrigation process occurs and the water passes through the soil body, Sparks (1998) indicated that this process leads to the dissolution of substances through exchange interactions between water and soil. In this regard, the Gapon equation indicates the distribution of ions at the exchange site, and that any loss or gain of an exchanged ion by the soil is accompanied by a loss or gain of another ion according to the Ratio Law. Calcium and magnesium are present in the soil in different forms (dissolved, exchangeable and non-exchangeable), the largest part is found non-interchangeably within the primary minerals and secondary clay minerals, and it is reported that the amount present in the secondary minerals is greater than in the primary minerals, as indicated by many researchers (Simard *et al*., 1992, Al-Uraibi, 2002, Al-Hadidi, 2012). Senbayeam *et al*. (2015) stated that the dynamic balance between the different formulas of calcium and magnesium in the soil system depends to a large extent on the mineral composition and these formulas are controlled by the processes of adsorption and desorption, and that any depletion of any formula will be compensated by the other formulas to form a new state of equilibrium. Sparks (2003) explained that the different forms of calcium and magnesium are in a state of dynamic equilibrium, and that any process of depletion of a particular

formula will be compensated by other formulas to form a new equilibrium state. Calcium results from the decomposition of many rocks and minerals in the soil, such as calcium carbonate and others. As for magnesium, its interactions behave similarly to calcium, and its concentration ranges from one-third to one-half of the concentration of calcium, and it may be equal to or more than it at times (Al-Omari, 2021). Glover (1996) confirmed that both calcium and magnesium easily form what is called the double ion, and this ion affects the solubility of carbonates, as it increases the amount of dissolved calcium carbonate and reduces precipitation. Al-Oraibi (2002) noted that there is a difference between the two ions of calcium and magnesium in terms of dispersion, and that the reason for the difference in the behavior of magnesium from calcium in this regard is due to the difference in the diameter of its mineralization, as the diameter of the mineralization of magnesium is greater than that of calcium. This means that the electrostatic force with which magnesium binds with colloids is less compared to calcium, and therefore the repulsion forces responsible for dispersion are greater in the system that contains magnesium compared to the system that contains calcium (Al-Obaidi, 2006). Nghimesh (2018) indicated that calcium is not easily washed out of the soil due to the tensile strength on the surfaces of soil colloids, and calcium is often the dominant Ca^{2} positive ion on the surfaces of soil particles. Calcium and magnesium ions prevail in the soils of arid and semi-arid regions, as in Iraqi soils, where there are calcium and magnesium salts such as chlorides and sulfates. As for the fate of calcium and magnesium in the soil, Ali *et al*. (2014) indicated that it is lost by leaching with irrigation water or rainwater in areas with a lot of rain. It is deposited in the form of carbonate or phosphate in the soil.

MATERIALS AND METHODS

1- Selection of study sites:

The study included sites for two soils of different order (Al-Mazara' and Bashiqa)within Nineveh Governorate - Iraq. Soil samples were collected from the surface depth (30 cm) to conduct routine analyses. The soil samples were air dried and ground, then sieved with a 2 mm sieve, The amount of clay, silt, sand, total calcium carbonate, organic matter, exchange capacity of positive ions, pH and electrical conductivity EC were estimated by the described methods, by the described methods (Carter and Gregorich, 2008). As shown in Table (1)

2. The effect of wetting and drying on calcium and magnesium equilibrium

Soil was taken naturally undistributed sample from the same sites mentioned above by columns, the length of the column is 25 cm and the diameter is 7 cm. The column was inserted into the soil to a depth of 15 cm. Filter paper was placed at the bottom of the column. The columns were moistened from the bottom with water according to the capillary property. Column weight $+$ soil $+$ water to represent W1, the columns were left to dry, then the column $+$ soil was weighed to represent W2, the difference between W1 and W2 represents the PV pore size. The experiment was carried out by adding two types of water (river water and well water as shown in Table 2). Water was added to each column with a volume equivalent to PV by weighing the column. Wetting and drying were alternated for ten cycles, and the period between one cycle and another was 10 days. Soil samples were taken after the first cycle, in the fifth and tenth cycles, the exchanged ions, the relative activity, and Gapon coefficient KG were measured after each cycle, and then the following kinetic equations were applied according by (Safarzadeh *et al.*, 2018)

1. Zero order equation $C_t = C_0 - K_t$ ………(1)

2. First order equation $\ln (C_0 - C_t) = \ln C_0 - Kt$ ……….(2)

1

- 3. Parabolic diffusion equation $C_t = C_0 Kt^2$ ……….(3)
- 4. Elovich equation $C_t = 1/K \ln C_0 K + 1/K \ln t$ ……….(4)
- 5. Power Function equation ln $C_t = \ln C_0 + K \ln t$ ………(5)

To determine the best equation, we relied on the lowest standard error (SE) and the highest determination coefficient (R²) (Simard *et al*., 1992)

Traits	Al-Mazara	Bashiqa	Unit
Bulk density	1.74	1.67	$gm.cm-3$
Porosity	34	37	$\frac{0}{0}$
Clay	31.45	28.55	$gm.kg^{-1}$
Silt	14	36.90	
Sand	54.55	34.55	
Texture	SCL	L	
Lime $(CaCO3)$	30.5	41.0	$gm.kg^{-1}$
Organic Matter (OM)	2.57	3.61	
Cation Exchange Capacity (CEC)	23.04	34.34	$Cmol.kg^{-1}$
Potential Hydrogen (pH)	7.50	7.72	
Electrical Conductivity (EC)	1.00	0.95	$dS.m^{-1}$
Calcium (Ca^{+2})	3.00	6.00	$meq.L^{-1}$
Magnesium (Mg^{+2})	2.00	2.00	
Sodium (Na^+)	1.12	1.04	
Potassium (K^+)	0.36	0.49	
Chloride (Cl ⁻)	1.16	0.07	
Bicarbonate $(HCO3)$	2.60	3.40	
Sulfate (SO_4^-)	1.03	1.78	

Table (2) : Chemical analysis of water used in the wetting process

RESULT AND DISCUSSION

The effect of the number of wetting and drying cycles on the behavior of calcium and magnesium in the study soils: In order to know the behavior, interactions and release of calcium and magnesium from the two soils of the study, the soil was moistened with ten successive cycles, as the soil was moistened with two types of water (river water and well water) for known the effect of the ionic strength of the water on the equilibrium of calcium and magnesium. The effect of the number of wetting and drying cycles on the exchange release of calcium and magnesium:

There was a difference in the amount of exchanged cations released from the solid phase of the soil according to the number of hydration cycles, as shown in Table (3). The first cycle was (15.4 and 18.38) mmol.¹⁻¹ in the soils of Al-Mazara' and Bashiqa, respectively, and the lowest values were in the tenth cycle and reached (9.95 and 15.91) in the soil of Al-Mazara' and Bashiqa , respectively. Regarding the magnesium released from the soil of Al-Mazara', its values ranged it ranged between (1.46 - 2.95) in the fifth and first cycle, respectively, while in the soil of Al-Mazara' its values ranged between (0.47 - 1.43) in the tenth and first cycle, respectively. When wetting the soil with well water, the highest value of calcium released from the soil of Al-Mazara' in the first cycle was (15.85) mmol. L^{-1} , and the lowest value was equal in the fifth and tenth cycles, as it amounted to (14.9), and in Bashiqa soil the highest values were also recorded in The first cycle (19.71) and gradually decreased in the fifth cycle, and the lowest value was in the tenth cycle (17.28), and with regard to magnesium released from the soil of Al-Mazara' the highest values were recorded in the first cycle (3.37) and the lowest values (1.90) appeared in the fifth cycle, while in Bashiqa soil, the highest values were also in the first cycle (2.37), and the lowest value was equal in the fifth and tenth cycles and reached (1.40).

When we compare the two soils of the study, we notice that the amount released from the exchanged calcium and magnesium ions in the Bashiqa soil was generally greater than the amount released in the soil of the Al-Mazara' when using both types of water. The use of the two types of water in the wetting process, and also there was a difference in the amount of exchanged cations release from the solid phase of the soil according to the difference in the ionic strength of the water used in the hydration process, as we note that the quantities of cations released from the two studied soils when wetting with well water were higher than the amount of cations released from them at wetting it with river water.

Ion	Al-Mazara		Bashiqa			
	River Water	Well Water	River Water	Well Water		
First Cycle						
$EX-Ca^{+2}$	15.4	15.85	18.38	19.71		
$EX-Mg^{+2}$	2.95	3.37	1.43	2.37		
Fifth Cycle						
$EX-Ca^{+2}$	14.44	14.90	17.91	18.75		
$EX-Mg^{+2}$	1.46	1.90	0.95	1.40		
Tenth Cycle						
$EX-Ca^{+2}$	9.95	14.90	15.91	17.28		
$EX-Mg^{+2}$	1.48	1.95	0.47	1.40		

Table (3): the exchangeable calcium and magnesium concentrations for the number of different hydration cycles in the two studied soils

Effect of the number of wetting and drying cycles on the relative activity of calcium and magnesium: Table No. (4) shows the effect of the number of wetting and drying cycles on the relative activity (RA) of each calcium and magnesium, and the results shown in the table show that there is a difference in the relative activity values between the two study soils and for the two types of water used in wetting, when the soil was moistened with river water, it was the lowest value of the relative activity value of calcium is (0.599) in the fifth cycle and the highest value (1.430) in the tenth cycle. This is for the soil of Al-Mazara'. As for Bashiqa soil, the highest value (1.499) appeared in the tenth cycle and the lowest value (0.963) was in the fifth cycle. As for the relative activity for magnesium, the highest value appeared in the soil of Al-Mazara' (0.666), while the lowest value was (0.399) in the fifth cycle, while the highest value appeared in Bashiqa soil in the fifth cycle (0.714) and the lowest value was recorded (0.499) in the tenth cycle. When wetting with well water, the relative activity (RA) values of calcium ranged from (1.00) in the fifth cycle to (1.333) in the tenth cycle of the farmer's neighborhood soil, while the values in Bashiqa soil ranged between (1.375 - 1.812) in the tenth and first cycles, respectively. The relative value of magnesium in the soil of Al-Mazara' gave the lowest value (0.666) in the tenth cycle and the highest value (0.928) in the first cycle, while the values in Bashiqa soil ranged between (0.571-0.812) in the fifth and first cycle respectively. When comparing the two soils of the study, we notice that the relative activity values of calcium and magnesium ions did not have a stable behavior in the soil of the study, that is, in some cycles, their values in Bashiqa soil are higher than their values in the soil of Al-Mazara', and in other cycles, the values were in a different way, that is, we did not find that there any clear difference between the two study soils in terms of the relative activity values. Regarding the effect of the ionic strength of the water used for wetting on the relative activity values of calcium and magnesium, we also did not see a clear stability in their values, as we note that the values of the relative activity of calcium from Bashiqa soil when wetting with well water were higher than wetting with river water in the first and fifth cycle, while in the tenth cycle Its value was higher when hydrated with river water. As for the soil of Al-Mazara' when wetting with well water, the relative activity value was higher than hydration with river water, while at the first and tenth cycles, the values were higher when wetting with river water, while the relative activity values of magnesium in Bashiqa soil were higher when wetting with well water in the first and tenth cycle While the value was higher when wetting with river water in the fifth cycle, and in Ai-Mazara soil, we notice that the relative activity values were higher when wetting with well water and for all cycles.

Table (4): The relative activity RA of calcium and magnesium for the number of different hydration cycles in the two studied soils

The effect of the number of wetting and drying cycles on the Gapone's constant KG for calcium and magnesium : Chaudhari and Somawanshi (2002) described the Gapone's constant KG as one of the chemical concepts that describe the cation exchange processes between the liquid and solid phases in the soil system, that is, there is a preference for one cation at the expense of another cation, and therefore it is called the concept of the Gapone's constant, as it deals with Table (5) The values of the Gapone's constant for calcium and magnesium in the two soils of the study, when the soil was moistened with river water, the highest value of the Gapone's constant for calcium in the soil of Al-Mazra' was (24.10) in the fifth cycle, and the lowest value (6.95) was in the tenth cycle, while in Bashiqa soil the values ranged from (10.61) In the tenth cycle to (18.59) in the fifth cycle, as for the Gapone's constant for magnesium, it followed the same behavior in both soils, as the highest values appeared in the first cycle (4.42 and 2.20) for the Al-Mazraa and Bashiqa soils, respectively, and the lowest values were recorded in the tenth cycle (2.58 and 0.94) for both soils in respectively, and when the soil was moistened with the well water, the results had a slight to moderate difference, as we note from the table that the values of the Gapone's constant for calcium in the soil of Al-Mazara' ranged between (11.17 - 14.90) in the tenth and fifth cycles respectively, while the values in Bashiqa soil ranged between (10.87 - 13.13) in the first and fifth cycles respectively, and with regard to the Gapone's constant for magnesium, the highest values in the soil of Al-Mazra'a reached (3.36) in the first cycle, while the lowest (2.12) appeared in the fifth cycle, and in Bashiqa soil the values ranged from (2.24) in the tenth cycle to (2.91) in the first cycle, and when we make a comparison between the two soils of the study, we notice that the Gapone's constant KG for calcium and magnesium ions did not have a stable behavior in the soil of the study, that is, in some cycles, its values in Bashiqa soil are higher than their values in Al-Mazara soil, and in other cycles the values were in a different way, that is, we did not find that there any clear difference between the two study soils in terms of the values of Gapone's constant. Regarding the effect of the ionic strength of the water used for humidification on the values of the Gapone's constant for calcium and magnesium, we also did not see a clear stability in the values. As we noticed that the values of Gapone's constant for calcium behaved completely differently from the behavior of the relative activity RA of calcium in the two soils of the study, as the values of Gapone's constant for calcium in Bashiqa soil when wetting with river water were higher than wetting with well water in the first and fifth cycle, while in the tenth cycle its value was higher when wetting with well water, as for the soil of Al-Mazara' when wetting with well water, the value of the Gapone's constant for calcium was higher than that of hydration with river water at the first and tenth cycles, while the values were higher when wetting with river water in the fifth cycle, while the values of Gapone's constant for magnesium in Bashiqa soil were higher when wetting with well water in the first, fifth and tenth cycle, while the values in the soil of Al-Mazara' were higher when wetting with river water in the first and fifth cycle, with the exception of the tenth cycle, the values were higher when wetting with well water.

Table (5): The Gapone's constant KG of calcium and magnesium for the number of different hydration cycles in the two studied soils

Soil system, in addition to the occurrence of dissolution of some minerals that carry each cation, which affects the value of Gapone's constant for ions (Sposito, 2008), and low values of Gapone's constant indicate the low capacity for ion adsorption, unlike soils with high values, which express sites with high binding energy for each any cation that participates in the exchange reactions that occur between calcium and magnesium ions (Al-Mohamdani, 2008).

Mathematical description of the reactions of calcium and magnesium as a function of time Kinetic equations were used to describe the process of released and transfer of calcium and magnesium from the two studied soils as a result of wetting the natural columns of the soil under study with two types of water (river water and well water), where the amount of released ionic species and concentrations in equilibrium filters were used as a function of time and to find the best equation that describes the mechanism of liberation and transfer. The kinetic equations used in our study are zero-order equation, first-order equation, diffusion equation, Elovich equation, and power function equation, and the values data indicate that most of the points of calcium and magnesium values lie on these lines, and this indicates the validity of using all kinetic equations in the process of describing interactions, and this was confirmed by the results of the statistical analysis presented in tables (6) which indicated the existence of a significant statistical correlation between the ionic types released with the desorption time, that is, all the kinetic equations gave a good description of the desorption and transport of calcium and magnesium ions, as all the determination coefficient values were high for all equations and in both soils, which ranged from (0.878 to 0.999) for the calcium ion and from (0.797 to 0.797). 0.999) for the magnesium ion, which leads us to the possibility of using any of the mathematical equations mentioned above.

In order to know the best equation, the highest determination coefficient (R^2) and the lowest standard error (SE) were relied upon. The order of the equations according to their preference was as follows:

Calcium ion Ca⁺²: power function equation > diffusion eq. > Elovich eq. > zero order eq. > first order eq.

Magnesium ion Mg^{2} : power function eq. > Elovich eq. > diffusion eq. > zero order eq. > first order eq.

The power function equation was the most efficient in describing the relationship between the release of calcium and magnesium ions and the reaction time, because it has the highest coefficient of determination \mathbb{R}^2 and the lowest standard error SE (table 6) and figure (1).

Figure (1) : Kinetics of Ca and Mg according to Power Function eq.

Since this equation shows the logarithmic relationship, and its superiority indicates that the relationship between the amount and rate of the desorption ion is proportional to its quantity in the solid phase in the soil and that there is more than one processing source for these ions. Therefore, the liberation process is expressed according to this equation as a multi-order reaction (Al-Sultan, 2022). This means that the relationship is a curvilinear relationship and states that the amount released of the ion is directly proportional to the reaction time raised to a certain exponent, meaning that the desorption process of the ion is determined by the reaction time (Sparks, 2003). In this regard, many researchers have indicated (Al-Obeidi and Al-Zubaidi, 2001; Shams Al-Din, 2017) who confirmed the validity of this equation in the mathematical description of the desorption of ions.

CONCLUSION

Dissolved and exchangeable calcium and magnesium values decreased with increasing number of wetting and drying cycles. The results of the kinetic study also showed the superiority of the exponential function equation in describing the desorption of calcium and magnesium in the soil with time among the kinetic equations used, which indicates that the relationship between the desorption of cations and time is logarithmic. The difference in the ionic strength of the irrigation water had an effect on the coefficient of desorption rate of calcium and magnesium. when wetting the soil with well water, it led to a clear increase in the values of the coefficient of desorption of ions from the soils of the study compared to wetting with river water.

CONFLICT OF INTEREST

The authors declare no conflicts of interest associated with this manuscript.

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