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Using the kinetic approach for the adsorption of base ions (Ca, Mg, Na, K) by the calm flow method in some soils in the northern of Iraq

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ABSTRACT

KEY WORDS:

Mineral Identification, Missible displacement, kinetic equations (Power, First order, Parabolic Elovage , Zero order).

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Four soils were selected from northern Iraq, within the ranks (Mollisols, Inceptisols) from the provinces of Dohuk, Erbil and Sulaymaniyah from different agricultural fields from the root zone (0-0.30 m). Their physicochemical and mineral properties were estimated to study thermally isotherm adsorption by the calm flow method of soil columns using an electrolytic solution. At concentrations of (3) mmol charge.L⁻¹, containing Ca, Mg, K, and Na ions in two repetitions at a constant temperature of approximately 298 ± 2 K. equilibrium leachates were collected in which the ions were estimated according to the coefficients. The results indicated that the reactions ranged from medium alkaline to medium acidic. (6.7- (7.8), unaffected by salinity (1.44 - 0.29) dS.m⁻¹ with an ion exchange capacity between (22.43 - (33.9 Cmolc.Kg⁻¹) and is calcareous soil due to its high content of total carbonate minerals (-112) g.kg⁻¹. In addition to the calcareous origin material, and it has a high clay content (304-534) g.kg⁻¹ with the predominance of smectite, chlorite, Illite, kaolinite and Illite clay minerals, the nature of ion exchange using the kinetic entrance of adsorption showed a clear effect of the porous fats and the contact time of the electrolyte solution on the adsorbed quantities depending on the type of soil. Show the mathematical description of the process of arranging the kinetic equations according to their validity as follows: Power > First order > Parabolic > Elovage > Zero order.

استخدام المدخل الحركي لامتزاز الايونات القاعدية الكالسيوم , المغنسيوم , الصوديوم والبوتاسيوم بطريقة الجريان الهادئ في بعض ترب شمالي العراق

قارمان قادرمولود سيان و محمد علي جمال العبيدي
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الخلاصة

اختيرت اربعة ترب من شمال العراق. ضمن رتبي (Inceptisols , Mollisols) من محافظات دهوك , اربيل وسليمانية من حقول زراعية مختلفة من المنطقة الجذرية (0-0.30 م). قدرت صفاتها الفيزيوكيميائية والمعدنية لدراسة الامتزاز المتماثل حراريا بطريقة الجريان الهادئ لاعمد ترب باستخدام لمحلل اليكتروليتي بتراكيز (3) مليمول شحنة. لتر⁻¹.¹ يحتوي ايونات Na K, Mg, Ca بمكررين على درجة حرارة ثابتة تقريبا 298 ± 2 كلفن جمعت رواشح الاتزان قدر فيها الايونات حسب المعاملات. وقد اشارت النتائج الى ما يليذات تفاعل يتراوح بين متوسطة القاعدية إلى متوسطة الحامضية. (7.8 6.7-) , غيرمتاثرة بالملوحة (1.44 - 0.29) $d.s.m^{-1}$ ذات سعة تبادل ايوني بين (33.9 - 22.43) $Cmol_c.Kg^{-1}$ وتعد ترباً كلسية لارتفاع محتواها من معادن الكربونات الكلية (112-) $g.kg^{-1}$ فضلاً عن مادة الأصل الكلسية. ولها محتوى طيني مرتفع (534-304) $g.kg^{-1}$. مع سيادة معادن اطيان السميكتايت والكلوريت الايلايت والكاولينيت والإيلايت. بينت طبيعة التبادل الايوني باستخدام المدخل الحركي للامتزاز تأثيرا واضحا للجحوم المسامية ومدة تماس المحلول الكتروليتي على الكميات الممتزة باختلاف نوع التربة مما أدى إلى اختلافات كبيرة في كمية الامتزاز للأيون الواحد ومعامل سرعة الامتزاز. اظهر الوصف الرياضي لعملية ترتيب المعادلات الحركية وفق صلاحيتها كالاتي:

$$Zero\ order < Elovage < Parabolic < First\ order < Power$$

INTRODUCTION

Given the importance of soil ecosystems, as they are often used as reservoirs for the added chemical and organic fertilizers of various kinds, it was necessary to know the dynamics of geochemical processes in these systems that regulate the processes of transformation of these components and their fate. As (Bilias and Barbayiannis, 2017) showed that these ions can be sequestered in soil ecosystems through interactions: (Adsorption), (desorption), (Precipitation), and Complexation). The adsorption process is a superficial phenomenon characterized by solid surfaces, and with an increase in the surface area of the colloids, the adsorption process increases, and clays and organic matter, with a high surface area, increase the adsorption process depending on the polarity and nature of the active aggregates, and the type and size of the pores and gaps on its surface, as well as It's surface area (Selim, 2013 and Sparks, 2017) as charged surfaces tend to adsorb the most polar components in the solution. The surface area of the adsorbent material is of two types. The first type is the apparent external surface area of the adsorbent surface. The second type is an internal surface area that represents the walls of the internal pores that are within the adsorbent surface. Adsorption depends a lot, especially the physical one, on the surface area. Thus, the large surface area of the adsorbent material gives a greater adsorption capacity. Also, the arrangement and size of the pores on the surface of the passing material are of great importance to the efficiency of Adsorption, which increases when the size of the pores is greater than the size of the adsorbed particles because this allows these particles to flow into the pores and thus can occupy a larger surface area. On the contrary, the adsorbed particles will be hindered and prevented from penetrating into the pores. Kinetics is concerned with studying and understanding the reaction process and measuring the reaction speed of the reactants and depends on several factors, including the contact area between the materials, their concentrations, and the temperature of the system in which the reaction takes place (Sparks, 2017). Kinetics studies also give a deep knowledge of the pathways of Chemical reactions as well as the mechanisms of those interactions, many researchers explained that the

use of the chemical kinetics approach can provide a good description of the adsorption of ionic species by introducing the time factor with the amount of adsorption and describing it quantitatively with mathematical equations, as well as for the shift from traditional standards to standards Kinetics when measuring ionic species to make recommendations for soil management. (Elbana *et al*, 2018), indicated the possibility of conducting adsorption kinetics experiments, experimentally, in two different ways. Representation of the movement of the solute in the soil, under field conditions compared to the first method, as it is more suitable for rapid reactions in soil and mud. In addition, this technique can be applied more easily, and samples that may be washed for a long time do not need continuous monitoring. It was shown (Jalali *et al.*, 2020) that all the particles in the miscible displacement method may not be subject to interference with the adsorbent (Sorbate), and that the adsorption capacity may be less than the true estimate and may occur in a thin film. (Strawn *et al*, 2015) It has been shown that studies using the displacement method evaluate both the adsorption and diffusion of an adsorbent in an open system.

MATERIAL AND METHODS

Sample collection and preparation: Soil samples were collected from different agricultural fields in the governorates of Dohuk, Erbil and Sulaymaniyah in northern Iraq, from the root zone (0-0.30 m), and their geographical locations (GPS) are recorded in Figure (1) and Table (1). The samples were brought to the laboratory and air-dried, then ground and sifted with a sieve with a hole diameter of (2 mm) and mixed well and kept in plastic boxes for analysis. The physicochemical properties of the soil were estimated according to (Salim and Ali 2017) the methods mentioned in presented in the Tables (2). The soil classes (the size distribution of soil particles) were estimated using the hydrometer method described in (Gee and Bauder, 2002).

Table1. Shows the study area and sampling location

Soil	Location	Elevation/m	Longitude	Latitude
1	Atrush	975	43.35812	36.85269
2	Girtik	798	44.3036	36.1200.4
3	Mangesh	944	44.17354	36.23143
4	Maxmur	243	43.61722	35.59473

Mineral analysis of the clay of the study soils according to (Jackson, 1979) by removing the dissolved salts by washing with distilled water several times. And carbonate minerals using a solution of (1) Molar sodium acetate CH_3COONa With a reaction degree (5) acidified with glacial acetic acid. And the organic matter using hydrogen peroxide H_2O_2 6%. and iron and aluminum oxides according to the DCB method (Sodium dithionite citrate bicarbonate) proposed by (Mehra and Jackson 1960).

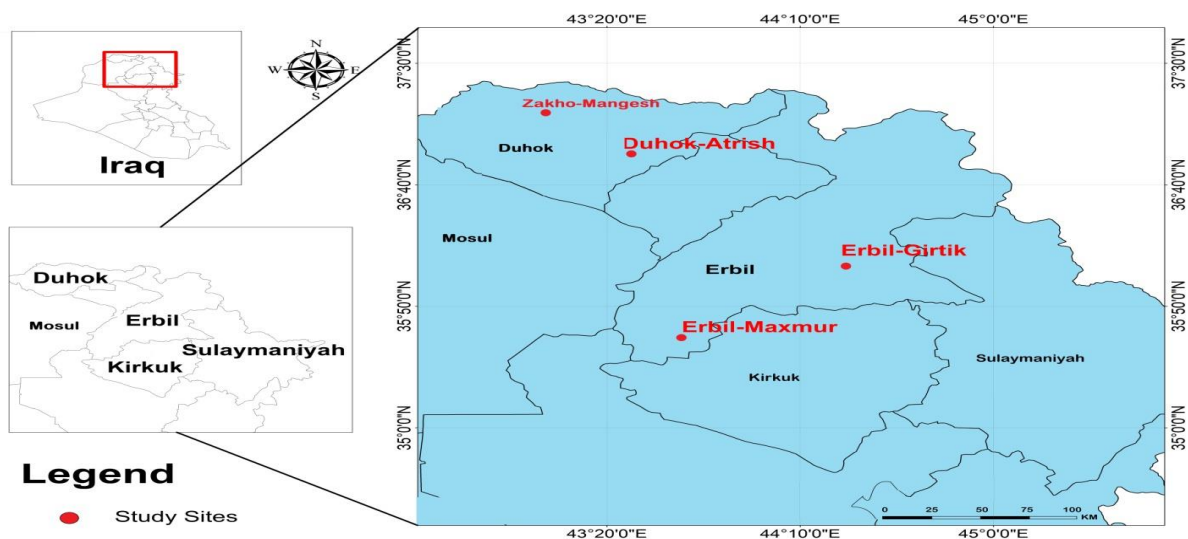


Figure 1. Shows soil samples that included the area of the study according to the GPS.

With (1) Molar potassium chloride, two slides were prepared from it. The sample saturated with magnesium was treated with 10% ethylene glycol vapor and the sample saturated with potassium was heated at 550C°. Conducting the mineral behavior examination using an X-ray diffractometer, Philipas model PW 1730. The method (Brindly and Brown, 1980) was used to diagnose clay minerals from X-ray curves by calculating the values of the distance between crystal networks (d-spacing). minerals in terms of (2θ) to determine their diffraction angles (Brown, 1961).

The X-ray machine (XRD) was used in the diagnosis of minerals according to the following standards for the device located in the General Company for Geological Survey and Mining located in Baghdad

Type: XRD Philips 1730 PW

Tube: Cu K_α Filter: Ni- Current: 30 mA - Rang of 2θ: 0-20-, 0-50. Wave length: 1.541838 Å

The values of the adsorbed ions were calculated according to the following equation:

$$M_{ad} = (M_{in} - M_{fin}) \times V/S$$

M_{ad}= Adsorbed ionic species, M_{in}= The concentration of the primary ionic species added, M_{fin}= The final ionic species concentration in the equilibrium solution (mmole_C.L⁻¹).

V= The volume of the equilibrium solution (Litre) , S= soil mass (Kg). According to the following kinetic equations (zero-order equation, first-order, second-order, Elovich, diffusion equation) in the following linear form:

$$\text{Zero order-- } C_t = C_0 - K_t$$

$$\text{First order-- } \ln(C_0 - C_t) = \ln C_0 - K_t$$

$$\text{Parabolic--- } C_t = C_0 + K_t^{1/2}$$

Elovich -- $C_t = a + K \text{Lnt}$

Power --- $\text{Ln}C_t = \text{Ln}C_o + K\text{Lnt}$

Where C_t represents the amount of ionic species adsorbed in centimoles. kg^{-1} at time t .

C_o represents the amount of ionic species adsorbed at time infinity, which can be calculated from the following equation:

$$\frac{1}{C_t} = \frac{1}{C_o} + b \cdot \frac{1}{t}$$

And by taking the reciprocal of the value of the secant in the above equation, C_o . can be obtained.

In order to determine the best mathematical equation to describe the ionic adsorption process, the coefficient of determination R^2 between the ionic adsorption index and time was calculated for each equation, then the standard error (SE) was calculated according to the equation:

$$SE = \left[\sum (C_* - C_a)^2 / n - 2 \right]^{1/2}$$

Where C^* : represents the measured ionic species, C_a : the amount of ionic species calculated from the equation, n : the number of measurement times after which the best mathematical equation was determined based on the highest value of the correlation coefficient and the lowest standard error according to the method (Sparks, 2002).

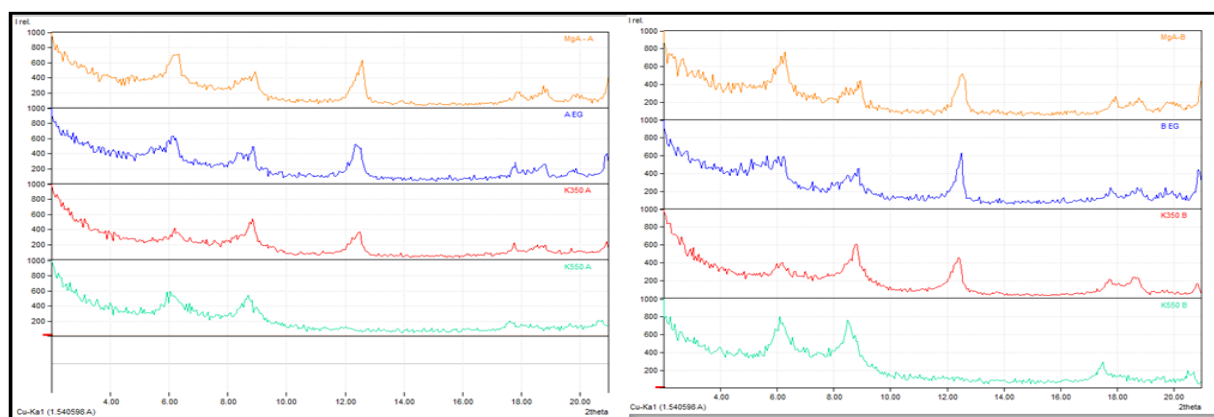
RESULTS AND DISCUSSION.

Physicochemical and mineral properties of the adsorption phase Components of the solid phase responsible for adsorption. Four soils were selected and classified within the ranks (Mollisol - Aridsol). The components of the solid phase differ from the ion adsorption process if the clay values differed from (369-534) and soil organic matter SOM (1.86-3.95) and CaCO_3 (114.00-405.11) g.Kg^{-1} And the type of clay minerals that were according to their sovereignty in the following order: smectite, chlorite, illite, kaolinite, and Illite, as shown in the table, with different percentages from one location to another, and as shown in Table (2), where the number of minerals was calculated by the semi-quantitative method, depending on the intensity of the peak, estimated to be in mm.

Table (2). values of mineral type and semi-quantitative distribution of clay minerals in the studied soils.

Soil	Location	Class	pH	Mineral					CaCO ₃	Clay g.Kg ⁻¹	SOM
				Pa	K	I	Ch	S			
1	Dhuk-Atrush	Mollisols	6.8	+	+	+	++	++++	212.5	410	3.85
2	Erbil-Girtik	Mollisols	7.2	+	+	+	++	++++	114	369	1.86
3	Zaxo-Mangesh	Mollisols	7.3	+	+	+	++	++++	225.5	425	3.95
4	Erbil-Maxmur	Inceptisols	7.8	+	++	++	+++	++++	405.11	534	2.44

It is noted from the figures (2) for sites (6, 8, 13, 33) that the smectite minerals are dominant. Smectite, Chlorite, Illite, Kaolinite, and PalygorsKite. When comparing the mineral composition of clay minerals between the study soils, it is noted that there are wide changes in the quantity and quality of the prevailing clay minerals in the study areas, whose presence rates varied from one site to another (Al-Obaidi, 2019). As shown in Table 2 and Figure 2 the presence of smectite in clay samples and its saturation with potassium and heating to (550 C°) led to a deterioration of the diffraction (14 A°) of the smectite mineral to a diffraction of (8.5-9.8 A°), which indicates that the mineral has a high layer charge and that it is inherited from weathering.



Figure(2) X-ray diffraction (XRD) of clay lozenges in Atrush 1 and Girtick 2

The smectite minerals in those soils are originally inherited in mica minerals and are characterized by their characteristics in terms of stabilizing and displacing potassium ions, and smectite has a high external charge, and this was confirmed by the studies (Al-Watifi, 2017), As showed in Figure (3) that the smectite minerals are of the type of high charge originating from mica minerals in most Iraqi soils (Al-Shamari, 2020). It confirms the presence of smectite minerals with a high external charge and also confirms that smectite minerals are originally inherited in mica minerals and are characterized by their characteristics in terms of stabilizing and displacing the potassium ion within its inner layers. The continued presence of diffraction AA (14.49 A°) in all treatments, which was accompanied by its third diffraction AA (4.72 A°), confirms the presence of real heat-resistant mineral chlorite. While the continued presence of diffraction AA (10.04 A°) within all treatments confirms the presence of mica minerals in the sample, the appearance of the second diffraction AA (5.01A°) with weak intensity and its continued presence in all treatments confirms that the mica minerals present are of the triple

mica type. Trioctahedra mica, represented by the mineral Biotite. The presence of diffraction aa (11.19, 12.26, 13.59 $\text{\AA}^\circ$) within the distance between the diffractions aa (10.04 $\text{\AA}^\circ$) and (14.49 $\text{\AA}^\circ$) representing the irregular stratified mineral (mica - smectite) confirms that the mica minerals have gone through different stages of weathering and transformation towards Smectite minerals 2:1 expanded (Al-Shamari, 2020).

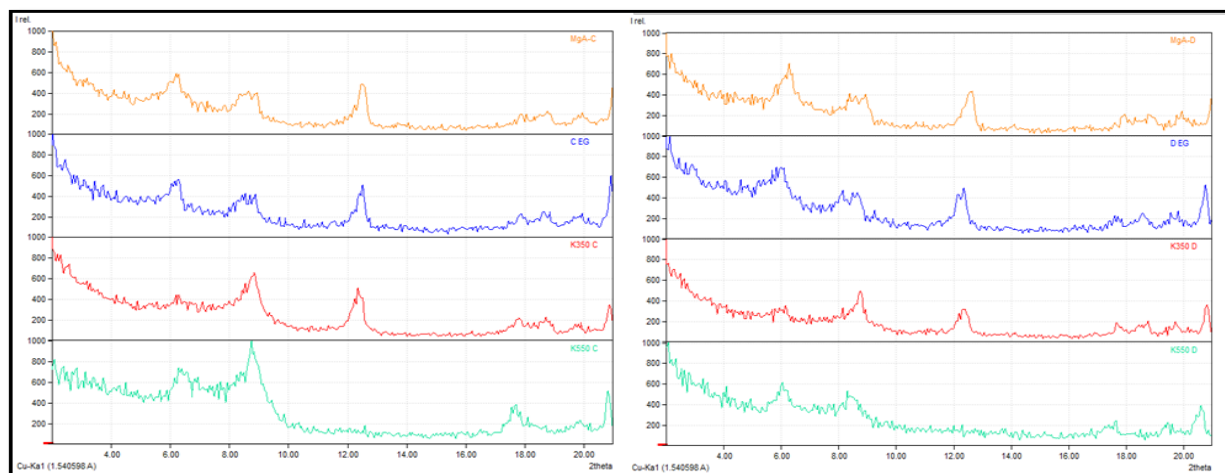


Figure (3) X-ray diffraction (XRD) of clay lozenges in Zakho 3 and Makhmur 4 regions

The course of the ion adsorption process in terms of the pore volumes of the running water, Figures (4) show the curves of the path of the ion adsorption process for the studied soil samples, in terms of the porous volumes of the running water, that there is a general trend for the behaviour of these curves achieved in increasing the amount of the ion adsorbed, collectively with the increase in the porous volumes passing through the soil column, but this increase is gradually decreasing in all study soil samples

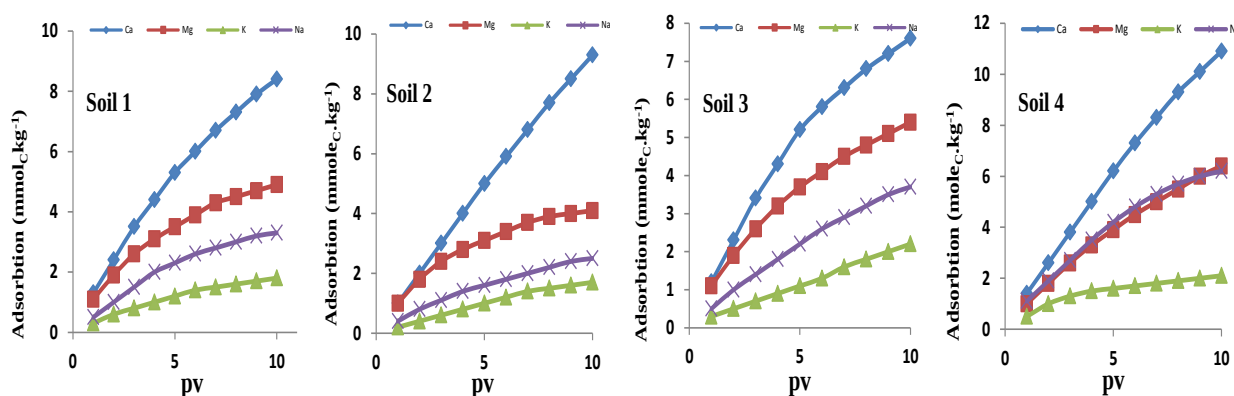


Figure (4) curves of the path of the ion adsorption process for the studied soil samples.

Must be noted that the flow of water in the soil columns is a calm flow that plays an important role in filling the gaps between the pores of the soil, which works to bring about processes (hydrolysis, positive ion exchange within the structural composition of mica at normal

temperatures, and the effectiveness of the hydrogen ion). (Wang *et al*, 2017), then the subsequent water flow will lead to the new water replacing the pore water filled with the remaining ions after adsorption and pushing it towards the bottom of the column and displacing it to the outside with a piston movement (Pistil Flow), quietly leaving behind voids and soil pores full of new water (Al- Obaidi *et al*, 2011). This will allow the interaction of more of the ionic type with the solid phase during the processes of hydrolysis and ion exchange and the effectiveness of the hydrogen ion (Ghosh and Debnath 2010) and the continuation of the mixing process and the quiet displacement of water with the soil body will lead to more ions in quantities less than the beginning of adsorption, which earns the adsorption curve A curvature towards the horizontal line in the Figures (4), especially after the eighth pore size, which clearly indicates (the electrolytic effect on the pressure on the electric double layer, and also shows the ability of the non-electrolytic water because of its positive and negative ions in the adsorption process by occupying the exchange sites on the surfaces of Clay and organic matter, as calcium, magnesium, potassium and sodium ions compete on the surfaces of the exchange complex and displace the latter towards the soil solution. The effect of the contact time of the electrolyte solution on the adsorbed quantities.

The results showed in Table (3) that the duration of contact of the adsorption solution with the soil surfaces differed according to the type of soil from time (36-123) and from (28-108) and (35-124) and (38-151) minutes for sites (1, 2, 3 and 4), respectively, which led to significant differences in the amount of adsorption for one ion, as the amount of the type of ion adsorbed increased from (13-84) (10-93) (12-76) (14-109) calcium and from (11-49)) (10-41) (11-54) (10-64) for the magnesium ion and from (3-18) (2-17) (3-22) (5-21) for the potassium ion and from (5-33), (4-25), (5-37), (11-62) mmolcKg⁻¹ of the Na ion for the four soils, respectively. This indicates the difference in the ability of soils and their strong tendency towards the adsorption of the four cations ions, and the reason for the difference in the amount of the ionic species adsorbed is attributed to some physicochemical properties such as clay, quantity and quality, organic matter, and the exchange capacity of positive ions (Table 3) (Jain *et al*, 2004) and (Anil and Sanjay, 2016). It is noted from the results that the amount of adsorbed calcium and magnesium exceeded the amount of (sodium, and potassium) adsorbed, which indicates that these soils have a high preference for calcium adsorption, and this is consistent with what was found by (Basta *et al*, 2005). Kaolinite prefers the adsorption of calcium over magnesium. It is noted from Table (4-8) that kaolinite was the dominant mineral in the soil under study. Quiet mixing, while the second stage showed a slowdown in the rate of velocity and a slight increase in it (Al-Obaidi and Shams al-Din 2018). The reaction path gains a slight slope until these curves become almost parallel to the x-axis, indicating that the reaction system has reached a state of semi-equilibrium, but it does not reach the state of constant adsorption, which requires conducting subsequent studies by adopting more flowing pore sizes.

Table (3) the effect of contact time of the electrolyte solution on the adsorption of the four ionic species by the miscible displacement method

Soil	PV	Quantity of Ion mmoleC.kg-1				Tim min
	addition	Ca	Mg	K	Na	
1	1	6.5	5.5	1.5	2.5	36
	10	42	24.5	9	16.5	751
2	1	5	5	1	2	28
	10	46.5	20.5	8.5	12.5	638
3	1	5	5	1	2	28
	10	46.5	20.5	8.5	12.5	638
4	1	7	5	2.5	5.5	38
	10	54.5	32	10.5	31	936

According to the law of proportions (Abasiyan and Towfighi, 2018) through three. As shown in Figures (4-25) and (4-26) adsorption of ionic species with time by the two methods of meal and displacement of miscibility, shown in Figure (5) the difference in the number of ionic species adsorbed in different soils, and the discrepancy in the adsorbed quantities with the increase in ionic species added over time may be attributed to the occurrence of rapid saturation. The adsorption sites are limited and low in ionic adsorption, which can occur during the first minutes of the reaction time.

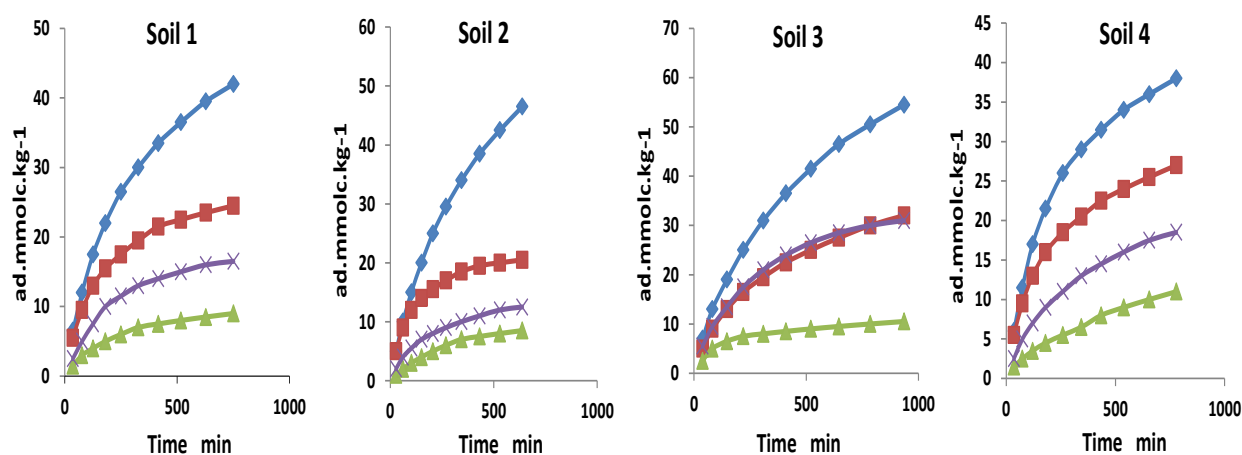


Figure (5) Adsorption of ionic species with time in the unsaturated study soil by the mixture displacement method

This leads to occupying most of the adsorption sites in the soil and decreasing their numbers, and after that, any increase in the added ion does not represent anything but pressure on the diffusion of part of the ionic type present in the solution, which constitutes a (compressive driving force) on the electric double layer.

Mathematical description of the adsorption process: The results are shown in Tables (4) and (5) kinetic equations to describe the adsorption of calcium, magnesium, potassium, and sodium by the binary exchange equilibrium and quiescent flow methods, which include the values of the coefficient of determination (R^2) and the standard error (SE). The results showed that All the equations gave a good description of the adsorption process through the high values of the coefficient of determination, and the best of them was the power function (exponential) equation, which gave the highest value of the coefficient of determination and the lowest standard error, while in the Figure (6) shown a rest of the kinetic equations were arranged according to their validity as follows: (Power equation > First order equation > Parabolic equation > Elovage equation > Zero order equation).

Table (4) The values of the root square and the standard error to choose the best mathematical description of the kinetic equations

Soil	Power		Elovage		Zero order		Parabolic		First order	
	R2	SE	R2	SE	R2	SE	R2	SE	R2	SE
1										
Ca	0.98	0.18	0.99	14.36	0.92	12.85	0.99	0.05	0.99	1.12
Mg	0.96	0.20	1.00	10.27	0.85	10.65	0.95	0.13	1.00	0.95
K	0.97	0.95	0.99	5.98	0.88	3.20	0.95	0.05	1.00	0.55
Na	0.95	1.16	0.99	8.38	0.85	6.00	0.95	0.07	0.98	0.88
2										
Ca	0.98	0.11	0.99	12.10	0.91	9.77	0.99	0.15	0.99	1.00
Mg	0.96	0.17	1.00	11.21	0.85	10.25	0.95	0.21	1.00	0.84
K	0.97	0.89	0.99	5.39	0.88	2.21	0.97	0.12	1.00	0.44
Na	0.95	0.28	0.99	9.30	0.85	4.25	0.95	0.04	0.98	0.65
3										
Ca	0.98	0.25	0.99	13.36	0.92	11.44	0.99	0.05	0.99	1.30
Mg	0.96	0.28	1.00	10.27	0.85	9.66	0.95	0.13	1.00	1.10
K	0.97	0.96	0.99	6.98	0.88	4.32	0.95	0.07	1.00	0.55
Na	0.95	0.92	0.99	9.38	0.85	6.55	0.95	0.09	0.98	0.87
4										
Ca	0.98	0.33	0.99	15.36	0.92	14.55	0.99	0.10	0.99	1.44
Mg	0.96	0.29	1.00	14.27	0.85	13.76	0.95	0.14	1.00	1.23
K	0.97	0.90	0.99	9.98	0.88	7.65	0.95	0.08	1.00	0.77
Na	0.95	0.98	0.99	11.38	0.85	9.99	0.95	0.09	0.98	0.94

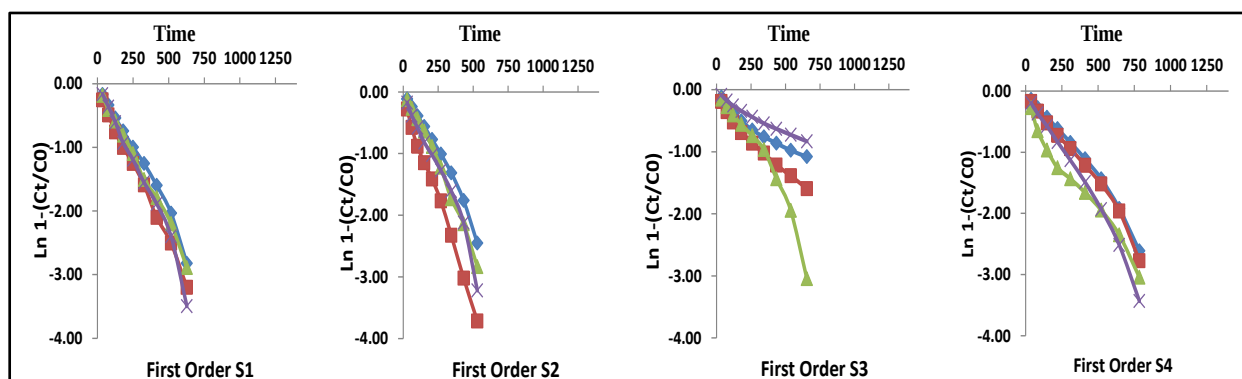


Figure (6) Adsorption curves of the four ionic species as a function of the reaction time according to the first order equation

The Power equation states that the amount adsorbed of an ion is directly proportional to the reaction time raised to a certain power (Sparks, 2003). However, it is an experimental equation that has no chemical implications

Table (5) Adsorption velocity coefficient according to the applied kinetic equations for the multiple adsorption system

Soil		Power	Elovage	Zero Order	Parabolic	First Order
			$\text{mmolckg}^{-1} \text{min}^{-1}$		$\text{mmolckg}^{-1} \text{min}^{-0.5}$	min^{-1}
6	Ca	0.528	16.116	0.123	0.034	-0.002
	Mg	0.533	12.64	0.222	0.026	-0.001
	K	0.642	125.675	0.084	0.039	-0.004
	Na	0.606	9.757	0.037	0.04	-0.005
8	Ca	0.755	29.601	0.132	0.047	-0.004
	Mg	0.459	10.948	0.045	0.037	-0.007
	K	0.734	5.562	0.024	0.047	-0.005
	Na	0.601	9.757	0.032	0.043	-0.006
13	Ca	0.603	30.2	0.103	0.036	-0.003
	Mg	0.477	16.99	0.057	0.034	-0.003
	K	0.569	4.648	0.014	0.027	-0.003
	Na	0.605	16.8	0.055	0.035	-0.004
33	Ca	0.702	34.321	0.094	0.046	-0.005
	Mg	0.626	19.265	0.048	0.044	-0.005
	K	0.434	5.215	0.02	0.034	-0.005
	Na	0.598	18.992	0.037	0.044	-0.002

Figure (6) shows that the first-order equation is of great importance because it is based on the principles of kinetic chemistry and explains the reaction mechanism in a quiet flow method on the principle of the diffusion process that controls the movement and transmission of the four ions between the layers of soil minerals (Zhang *et al*, 2020).

CONCLUSION

The kinetic input of adsorption by the quiet flow method showed a clear effect of the contact time of the electrolyte solution on the adsorbed quantities according to the type of soil and its clay mineral (Smectite, chlorite, kaolinite, and Illite), which led to large differences in the amount of adsorption for one ion. The mathematical description of the dual and multiple adsorption process has been arranged according to its validity as follows: Power > First order > Parabolic > Elovage > Zero order. The first-order equation is of great importance because it is based on the principles of kinetic chemistry and explains the reaction mechanism in a quiet flow method on the principle of the diffusion process that controls the movement and transmission of the four ions between the layers of soil minerals, *Ka* values according to first order greater divalent cation (Ca, Na) compering to mono-cation (Na, K) and ranging from (2-5),(1-7), (2-6) and (3-5) 10^{-3} for Ca, Mg, Na and K ions respectively.

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