

Kinetics of Potassium Release in Some Libyan and Egyptian Calcareous Soils

Nasseem, M. G.¹, A. H. Magda.¹, A. Z. Hussein¹ and A. A. Kamal²

¹ University of Alexandria, Faculty of Agriculture, Saba Basha, Alexandria, Egypt

² Department of Soil and water, Faculty of Agriculture, Omar El-mukhtar University, El-Beda, Libya

ABSTRACT

This work was carried out to investigate the kinetics of K release and its status in 12 Libyan and Egyptian calcareous soils. Different forms of K were determined in tested soils. The different extraction of the soil potassium forms pointed out that, soluble-K (0.75 and 0.61 mg K kg⁻¹ soil), exchangeable-K (32.4 and 28.81 mg K kg⁻¹ soil), nonexchangeable -k (337.60 and 311.92 mg K kg⁻¹ soil), mineral-K (4239.41 and 2516.54 mg K kg⁻¹ soil) and total-K (4610.00 and 2856.67mg kg⁻¹ soil) for Libyan and Egyptian soils respectively. The rate of potassium release was determined. The soil samples were equilibrated with 0.01 M CaCl₂ and 0.01 M oxalic acid for 1- 425 minutes. Plots of cumulative K released from different soils vs. time consisted of two parts, suggesting two different rates of K diffusion from soils. Three mathematical models (parabolic diffusion, power function, and Elovich equation) were used to describe cumulative K release. The Elovich and parabolic equations described the kinetics of K releases satisfactory in both the Libyan and Egyptian soils respectively indicating diffusion controlled exchange.

Key words: kinetic; release ; exchangeable; oxalic acid ; CaCl₂ ; Libyan and Egyptian.

INTRODUCTION

Potassium is a macro-element essential for plant growth and its importance in agriculture is well recognized. It plays an important role in several physiological processes in plant such as energy transfer, formation of sugars, starch and protein in plant (Darst, 1992 and Krauss, 1997). Potassium content in soils depends on the type of parent material and degree of soil mineral weathering. Soil K exists in four forms that are in equilibrium, each differing in its availability to crops. These forms, in decreasing order are: mineral, non-exchangeable (fixed or difficultly available), exchangeable, and solved (Havlin *et al.*, 2004).

The equilibrium reactions between K forms markedly affect whether applied potassium taken by plant, leached into lower soil layers or converted into un-available forms (Sparks and Huang, 1985). Knowing the equilibrium constants is very important for predicting the status and supply of potassium for plant (Lindsay, 1979). The nonexchangeable K is a source of K in some soils and can be released to provide a significant portion of the K removed by crops during the growing season (Mengel and Uhlenbecker, 1993 and Rahmatullah *et al.*, 1994). This interlayer K is also the major source controlling the long-term K supplying potential of soils (Cox *et al.*, 1999). Availability of nonexchangeable K is not dependent on

the quantity of interlayer K, but it depends primarily on the rate at which it can be released into more labile forms. The type of K-bearing minerals greatly affects on the release rate (Sparks, 1987).

The kinetics of potassium release determined by using different extraction methods have been used to study release of nonexchangeable K (Dhillon and Dhillon, 1990 ; Mengel and Uhlenbecker, 1993; Rahmatullah *et al.*, 1994; Ghosh and Singh, 2001; Benipal and Pasricha, 2002). These extractants include cation exchange resins (Dhillon and Dhillon, 1990), nitric acid (Gil-Stores and Rubio, 1992), organic acids (Zhu and Luo, 1993); electro-ultrafiltration technique (Rubio and Gil-Stores, 1996), salt solution (Lopez-Pineiro and Garcia Navarro, 1997 and Jalali, 2005) and sodium tetraphenyl boron (Cox *et al.*, 1999). Several equations have been used to describe potassium release kinetics including first-order, parabolic diffusion and Elovich (Jalali, 2005). However, few K release studies have been reported for calcareous soils. Therefore, more information is needed on the nature and rate of potassium release in calcareous soils. The objectives of this study were to investigate the kinetics of potassium release from some Libyan and Egyptian calcareous soils by using two different extractants and to use various kinetic equations to describe this release.

MATERIALS AND METHODS

Twelve soil samples were collected from the upper soil layer (0-30 cm) of the North Western Coast of Egypt (six samples) from different sites along the transects starting at km 50 Alexandria–Matruh, and six surface soil samples from different sites along the road extending from Tanamilo-South AL- Gabal EL -Akhdar Coast of Libya.

The soil samples were air-dried, ground, sieved (2 mm mesh) and the physical and chemical properties of these soils were determined according to the methods described by Page *et al.* (1982) and Jackson (1973) and the results obtained are presented in Table 1.

Different potassium forms: (i) water soluble (H_2O -K), (ii) potassium extracted by NH_4OAc (NH_4OAc -K), (iii) potassium extracted by nitric acid (Acid-K) and (iv) total-K were determined by the methods described by Pratt (1965). The mineral potassium concentration were estimated by subtracting the HNO_3 extractable potassium from total potassium (Parker *et al.*, 1989).

Kinetic of soil potassium release

The capacity of the soils for potassium release was tested through extraction with 0.01M $CaCl_2$ and 0.01 M oxalic acid according to Jalali and Zarabi (2006). Experimentally, 1.0 g soil was transferred with 20 ml of 0.01M $CaCl_2$ solution or 0.01M oxalic acid to a 50 ml glass bottle at about 25°C. The samples were then equilibrated on a reciprocating shaker at a

rate of 120 strokes min⁻¹ for intervals ranging from 1 to 425 min. (1, 5, 10, 15, 45, 75, 105, 135, 165, 195, 225, 255, 275, 305, 335, 365, 395 and 425 min.). At the end of the equilibrated period, the suspensions were filtered and the concentration of K in the supernatant was measured. The kinetics of soil K released for each treatment were described using the following equations (Sparks, 1995):

- Parabolic diffusion : $qt/q_0 = a + b t^{1/2}$
- Power function : $\ln qt = \ln a - b \ln t$
- Elovich equation : $qt = a + b \ln t$

Where qt is the cumulative K⁺ released at time t , q_0 is the maximum K released, a and b are constants, and t is time (min). These mathematical models were tested by least square-regression analysis to determine which equation best describes the K⁺ release from the soils. Standard errors of estimate (SE) were calculated by:

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

Where q and q^* represent the measured and predicted potassium released, respectively, and n is the number of data points evaluated. Potassium concentration in any solution was determined by flame photometry method. Analysis was replicated three times, and the results obtained are presented as means.

RESULTS AND DISCUSSION

Soil characteristics

As shown in Table 1, the tested soils were alkaline and mostly low in EC and organic matter. The equivalent calcium carbonate contents varied from 33.10 to 40.87% in the Libyan soils and from 22.54 to 39.82 % in the Egyptian soils. Clay contents ranged from 10.50 to 13.8% in Libyan soils and from 11.20 to 29.00% in Egyptian soils.

The average quantities of K forms (mg kg⁻¹ soil) in the soils (Table 2) were: as follows soluble-K were (0.75 and 0.61 mg K kg⁻¹), exchangeable-K were 32.4 and 28.81 mg K kg⁻¹, nonexchangeable-K were 337.60 and 311.92 mg K kg⁻¹; and mineral-K (4239.41 and 2516.54 mg K kg⁻¹) and total-K were 4610.00 and 2856.67 mgkg⁻¹ for Libyan and Egyptian soils respectively. On average, exchangeable-K were approximately 43.2 and 47.22 times higher than soluble-K, and the nonexchangeable-K was 10.42 and 10.82 times more than the exchangeable-K in Libyan and Egyptian soils, respectively.

Kinetics of potassium release

The cumulative amounts of K released versus time of extraction using 0.01 M CaCl₂ and 0.01M oxalic acid are presented in Fig 1, for both the Libyan and Egyptian soils.

It seems that the amount of K released was increased with increasing time of extraction. The trend in cumulative potassium release pattern was almost similar in 0.01M CaCl₂ and 0.01M oxalic acid. However, the total amount of K released into 0.01M oxalic acid was higher than that of 0.01M CaCl₂. The K released in 0.01 M CaCl₂ varied from 273.33 to 290.00 mg kg⁻¹ soil for Libyan soils and from 190.00 to 233.33 mg kg⁻¹ soil for the Egyptian soils. The corresponding release in 0.01 M oxalic acid were from 313.33 to 330.00 mg kg⁻¹ soil in Libyan soils and from 216.67 to 240.00 mg kg⁻¹ soil in Egyptian soils.

Potassium released by extraction with both extractants was summed and plotted against extraction time so that cumulative-release curves were obtained (Fig.2 for Libyan soils and Fig.3 for Egyptian soils). The patterns of the curves are related to the initial content of potassium. The curves indicate that there are two stages of release; (i) the first stage, which is at the beginning of the extraction, is characterized by extraction of soluble and weakly bonded potassium – mostly exchangeable, while (ii) the second stage (after about 50 minutes of extraction) is characterized by release of strongly bonded potassium—mostly the non-exchangeable form. The variations in the total amount of K released from different Libyan or Egyptian soil samples (Table 3) using CaCl₂ or oxalic acid extractants could be attributed to many factors such as particle size of K-bearing minerals and soil environment (Sparks and Huang, 1985). The nature of K-bearing minerals includes crystal structure, chemical composition, and degree of depletion and layer charge alteration (Hosseinpour and Kalbasi, 2002).

The variations in the quantities of K released from either 0.01M CaCl₂ or 0.01 M oxalic acid could be attributed to differences in their nature of chemical reaction with the soil. These soils may contain clay minerals which mean that there is surface edge, and interlayer sites that hold K. Potassium ions adsorbed on the planar surfaces are not specifically adsorbed, and the bond is relatively weak. Potassium ions in the interlayer are very strongly bonded and those at the edge sites take intermediate position, which means that the strength of bondage is not very high (Mengel, 1985). The Ca ions can exchange K ions on the surface and edge positions but due to its large size cannot easily exchange interlayer K. this is because the hydrated radius of Ca ion is 0.96 nm, thus Ca ions cannot replace K ions in interlayer sites easily. Thus, for Ca ion, more time is needed to replace K. As kinetic experiment continues, replacement of K with Ca results in an expansion of the clay mineral and the formation of edge sites contributing to the release of interlayer K.

The effect of oxalic acid on releasing K is attributed to the dissociated H ions and complexing organic ligands in the oxalic acid solutions. Simared et al. (1992) stated that extraction with oxalic acid involved very mild hydrolysis, ligand exchange, and complexation reactions. Thus, the increase in nonexchangeable K by 0.01M oxalic acid can be attributed to acidic conditions produced by adding oxalic acid which may have dissolved minerals present, exposing interlayer, and mineral K. In calcareous soils, of the present studies, Ca is the dominant cation. When oxalic acid is used, dissolution of calcite occurred which can provide a source of Ca and enhance replacing interlayer K. It is clear from Fig.1 for Libyan and Egyptian soils that the soils continued to release K through the period of reaction, indicating that equilibrium was not established even after 425 minutes.

Table 4 shows the values of percentages of CaCl_2 - K or oxalic acid-K (K-release capacity) of nitric acid - K (non-exchangeable potassium) for Libyan and Egyptian soils. The values ranged from 64.97 % in soil sample No.4 to 80.27 % in soil sample No.1, with an average value of 75.72% using CaCl_2 extractant and from 77.31 % in soil No.4 to 92.13 % in soil No.1 with an average value of 86.80 % using oxalic acid for the Libyan soils. Regarding the Egyptian soils, the values ranged from 57.53% in soil No.11 to 71.11 % in soil No.7 with an average value of 61.84 % using CaCl_2 as extractant and from 60.88 % in soil No.12 to 84.84 % in soil No.7 with an average of 68.69 % using the oxalic acid as extractant. These results indicate that after 425 minutes of extraction with 0.01 M CaCl_2 , or with 0.01M oxalic acid, a considerable portion of total nonexchangeable potassium was still remaining in most soils. This indicates that the unreleased, non-exchangeable potassium will be released and utilized by plants for a long period of time.

Three mathematical models; parabolic diffusion, Elovich, and power function equations were tested to describe the kinetics of potassium release for the Libyan and Egyptian soils and are shown in Fig. 2 (sample No. 1 and 4) and Fig 3 (sample No. 7 and 12) as representative soils. Table 5 revealed the determination coefficients (R^2), standard errors (SE) and parameters of the tested models. Based on the highest value of R^2 and the lowest value of standard error (SE) for the Libyan soils, Elovich equation satisfactorily describes the reaction rates of potassium release. However, parabolic equation could describe the release of potassium in the Egyptian soils using both extractants (0.01M CaCl_2 and 0.01M oxalic acid). Also, the Elovich equation could describe the release of K in the Egyptian soils. The obtained results agree with the findings of other researchers (Havlin and Westfall, 1985; Simard *et al.* 1992; and Al-Zubaidi and Al-Obudi, 2001). Hosseinpour and Kalbasi (2002) also reported that the kinetic release of potassium from different soils was well described by parabolic diffusion law, Elovich equation, and power function equations.

The constants *a* and *b* of each model represent the intercept and the slope of the linear curves resulting from plotting the released K^+ vs. time (Table 5). The constant *b* mirrors the release rate of the nonexchangeable K. The *b* values are known to correlate well with crop K released from the nonexchangeable K phase (Havlin and Westfall, 1985; and Mengel and Uhlenbecker, 1993). When plant uptake does not positively correlate with the *b* value, this may represent the soil's inability to meet the K demand by the crop. On the other hand, a high positive correlation can be an indication of adequate K release from the nonexchangeable K to meet the crop K needs. Out of the three models used to describe K release in the 6 samples of Libyan soils, the Elovich equation which demonstrated the best fit (R^2 and SE) and displayed the *b* values of 44.17 using 0.01M $CaCl_2$ and 50.34 0.01M oxalic acid (Table 5) which are in the order of magnitude in comparison of those obtained by Jalali (2005). On the other hand, the parabolic equation which demonstrated the best R^2 and SE for the Egyptian soils displayed the *b* values of 9.18 and 9.62 using 0.01M $CaCl_2$ and 0.01M oxalic acid, respectively. Generally, the Elovich and parabolic models had the best fit which is in agreement with Jalali (2006).

Mathematical analysis of potassium release data indicated that both the Elovich and parabolic diffusion equations had described potassium release kinetics in Libyan and Egyptian soils respectively. Fit of the data indicated diffusion control, and in all soils, it was characterized by an initial fast rate followed by a slower rate. Information obtained from mathematical models can help to explain the release mechanism(s) and estimate the potassium supplying power of soils.

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Table 1. The main chemical and physical properties of the used Libyan and Egyptian soils.

Site and Sample No	Location	pH (1:1)	EC dS/m (1:1)	O.M %	Total C aCO ₃ %	Water soluble cations meq/L				Particle size distribution (%)			Textural class
						K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Sand	Silt	Clay	
Libyan soils													
1	Tanamilo	7.98	0.50	1.23	34.34	2.17	1.74	1.60	3.6	55.10	34.40	10.50	Sandy Loam
2	Tanamilo	8.20	0.70	1.28	40.87	2.83	1.74	2.00	3.6	66.09	21.00	12.91	Sandy Loam
3	Tanamilo	8.10	1.10	1.26	33.10	2.65	1.96	4.20	3.8	62.50	26.25	11.25	Sandy Loam
4	Tanamilo	8.03	0.90	1.26	38.86	2.17	1.96	2.60	4.0	66.20	20.00	13.80	Sandy Loam
5	Tanamilo	8.35	1.70	1.29	36.94	2.67	1.30	3.40	4.0	71.50	15.90	12.60	Sandy Loam
6	Tanamilo	8.52	0.80	1.31	37.42	2.67	2.43	1.40	5.0	61.12	27.67	11.21	Sandy Loam
Egyptian soils													
7	Burg El-Arab	7.69	6.00	1.41	22.54	2.35	23.04	11.52	26.64	61.66	27.14	11.20	Clay Loam
8	Alowny sons	8.12	1.30	1.20	28.78	2.65	10.00	1.44	5.04	53.00	28.00	19.00	Loam
9	Ain Gzalla	7.91	5.10	1.26	32.62	2.15	37.39	5.40	7.20	53.46	30.30	16.24	Sandy Loam
10	El-Dabaa	7.94	1.30	1.08	27.34	2.5	9.13	3.78	5.40	52.98	32.90	14.12	Sandy Loam
11	Etnoh	8.28	1.20	1.29	39.82	2.15	2.90	7.92	4.68	37.00	38.00	25.00	Sandy Loam
12	Matruoh	8.37	0.90	1.30	38.86	2.83	4.00	1.62	4.32	31.00	40.00	29.00	Sandy Loam

Table 2. The quantities of different forms of potassium in the studied soils.

Sample No	Soil Location.	Soluble - K (mgkg ⁻¹ soil)	Exchangeable - K (mgkg ⁻¹ soil)	Nonexchangeabl e - K (mgkg ⁻¹ soil)	Mineral - K (mgkg ⁻¹ soil)	Total - K (mgkg ⁻¹ soil)
Libyan Soils						
1	Tanamilo	0.50	23.75	316.25	2919.50	3260.00
2	Tanamilo	0.85	37.40	349.27	5212.48	5600.00
3	Tanamilo	0.50	27.75	318.92	3392.83	3740.00
4	Tanamilo	1.15	39.60	386.07	5373.18	5800.00
5	Tanamilo	0.85	35.82	337.51	4285.82	4660.00
6	Tanamilo	0.67	30.08	316.59	4252.66	4600.00
	average	0.75	32.40	337.60	4239.41	4610.00
Egyptian Soils						
7	Burg El-Arab	0.50	21.25	245.42	1992.83	2260.00
8	Alowny sons	0.67	30.08	343.25	2566.00	2940.00
9	Ain Gzalla	0.50	23.75	315.67	2600.08	2940.00
10	El-Dabaa	0.50	23.75	262.92	2172.83	2460.00
11	Etnoh	0.67	31.83	345.84	2621.66	3000.00
12	Matruoh	0.83	34.92	358.41	3145.84	3540.00
	average	0.61	28.81	311.92	2516.54	2856.67

Table 3. Cumulative potassium released (mg kg⁻¹ soil) from soils using 0.01M CaCl₂ or 0.01M oxalic acid extractant.

Soil no.	0.01 M CaCl ₂	0.01 M oxalic acid
Libyan soils		
1	273.33	313.33
2	283.33	316.67
3	273.33	316.67
4	276.6	330.00
5	290.33	323.33
6	276.67	320.00
Average	278.94	320.00
Egyptian soils		
7	190.00	226.67
8	196.67	230.00
9	203.33	216.67
10	200.00	223.33
11	217.67	240.00
12	233.33	240.00
Average	206.83	229.45

Table 4 : The values of the percentage of CaCl₂ – K or Oxalic acid – K of Nitric acid – K in Libyan and Egyptian soils.

Soil no.	CaCl ₂ – K mgkg ⁻¹ soil	Oxalic acid – K mgkg ⁻¹ soil	Nitric acid – K mgkg ⁻¹ soil	$\frac{CaCl_2 - K}{Nitric\ acid - K} \times 100$	$\frac{Oxalic\ acid - K}{Nitric\ acid - K} \times 100$
Libyan soils					
1	273.33	313.33	340.5	80.27	92.02
2	283.33	316.67	387.52	73.11	81.72
3	273.33	316.67	347.17	78.73	91.21
4	276.67	330.00	426.82	64.97	77.32
5	290.33	323.33	374.18	77.59	86.41
6	276.67	320.00	347.34	79.65	92.13
Average	278.94	320.00	370.59	75.72	86.80
Egyptian soil					
7	190.00	226.67	267.17	71.11	84.84
8	196.67	230.00	374.00	52.59	61.49
9	203.33	216.67	339.92	59.82	63.74
10	200.00	223.33	287.17	70.80	77.76
11	217.67	240.00	378.34	57.53	63.43
12	233.33	240.00	394.16	59.20	60.88
Average	206.83	229.45	340.12	61.84	68.69

Table 5. Average of determination coefficients (R^2), standard error (SE) and parameters of the models used to describe potassium release to 0.01M CaCl_2 or 0.01M oxalic acid in the studied soils.

Kinetic model	Extraction media	a	b	R^2	SE
Libyan Soils					
Elovich ($y = a + b \ln t$)	0.01M CaCl_2	-2.03	44.17	0.98	12.20
	0.01 M Oxalic acid	8.55	50.39	0.99	10.72
Parabolic ($y = a + b t^{1/2}$)	0.01M CaCl_2	55.99	11.61	0.93	23.01
	0.01 M Oxalic acid	77.01	13.05	0.92	29.19
Power function $\ln K = \ln a + b \ln t$	0.01M CaCl_2	3.33	0.40	0.90	0.26
	0.01 M Oxalic acid	3.55	0.39	0.89	0.25
Egyptian Soils					
Elovich ($y = a + b \ln t$)	0.01M CaCl_2	-12.48	33.18	0.92	16.45
	0.01 M Oxalic acid	0.44	35.08	0.93	16.07
Parabolic ($y = a + b t^{1/2}$)	0.01M CaCl_2	25.62	9.18	0.98	8.59
	0.01 M Oxalic acid	41.70	9.62	0.97	10.02
Power function $\ln K = \ln a + b \ln t$	0.01M CaCl_2	2.98	0.40	0.96	0.13
	0.01 M Oxalic acid	3.44	0.33	0.96	0.10

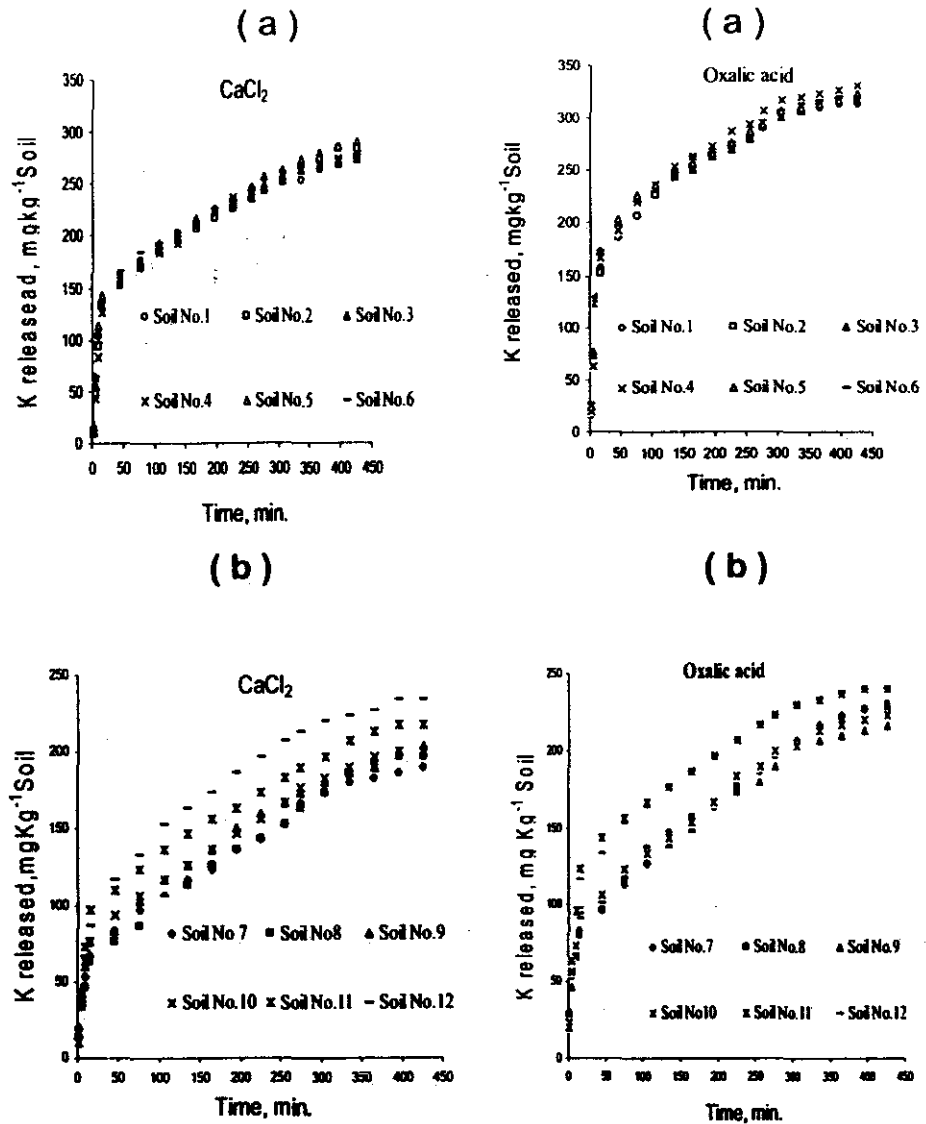


Fig. 1. Cumulative of K release with time by using 0.01M CaCl₂ or 0.01M oxalic acid extractants for the Libyan (a) or Egyptian soils(b).

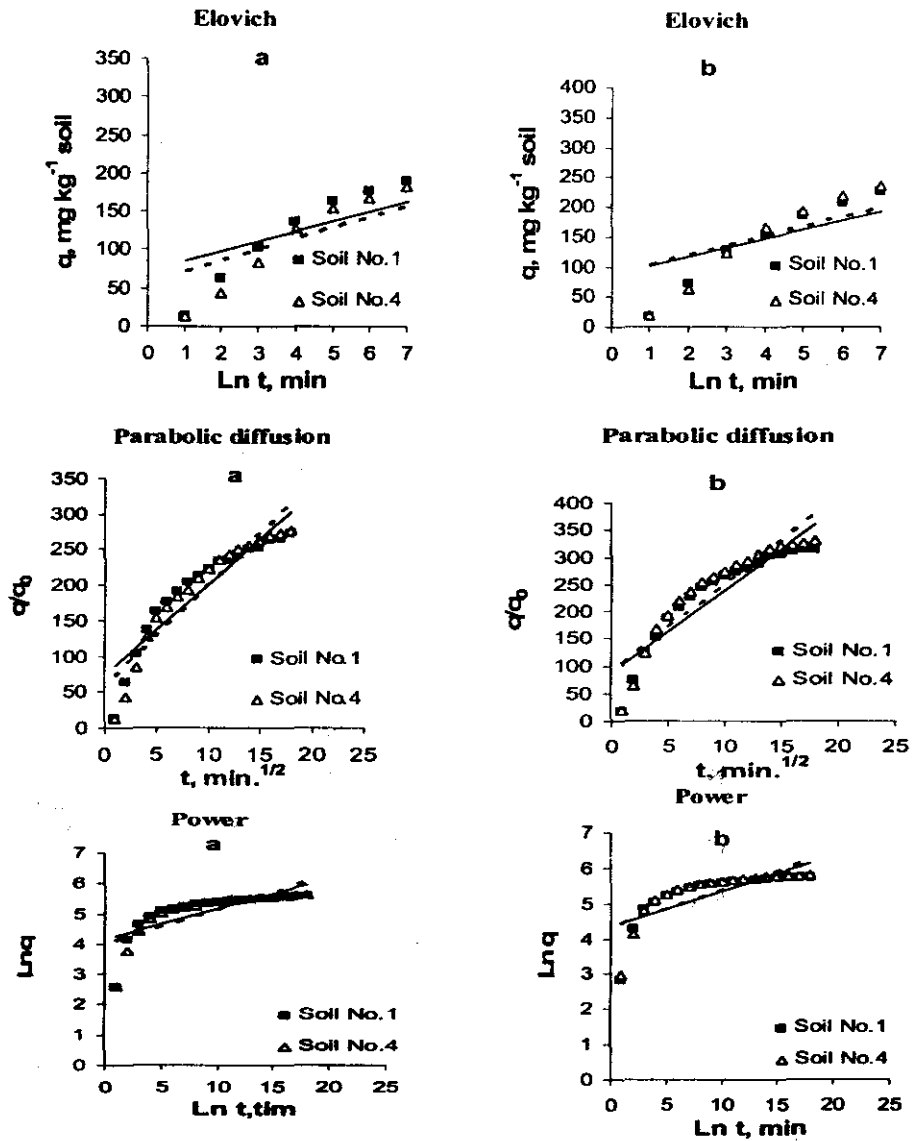


Fig.2. Relationship between the time and released K with 0.01 M CaCl₂ (a) or 0.01 M Oxalic acid (b) solution as described by three mathematical models in the Libyan soils.

Note: q : The cumulative K released and q_0 : The maximum K released.

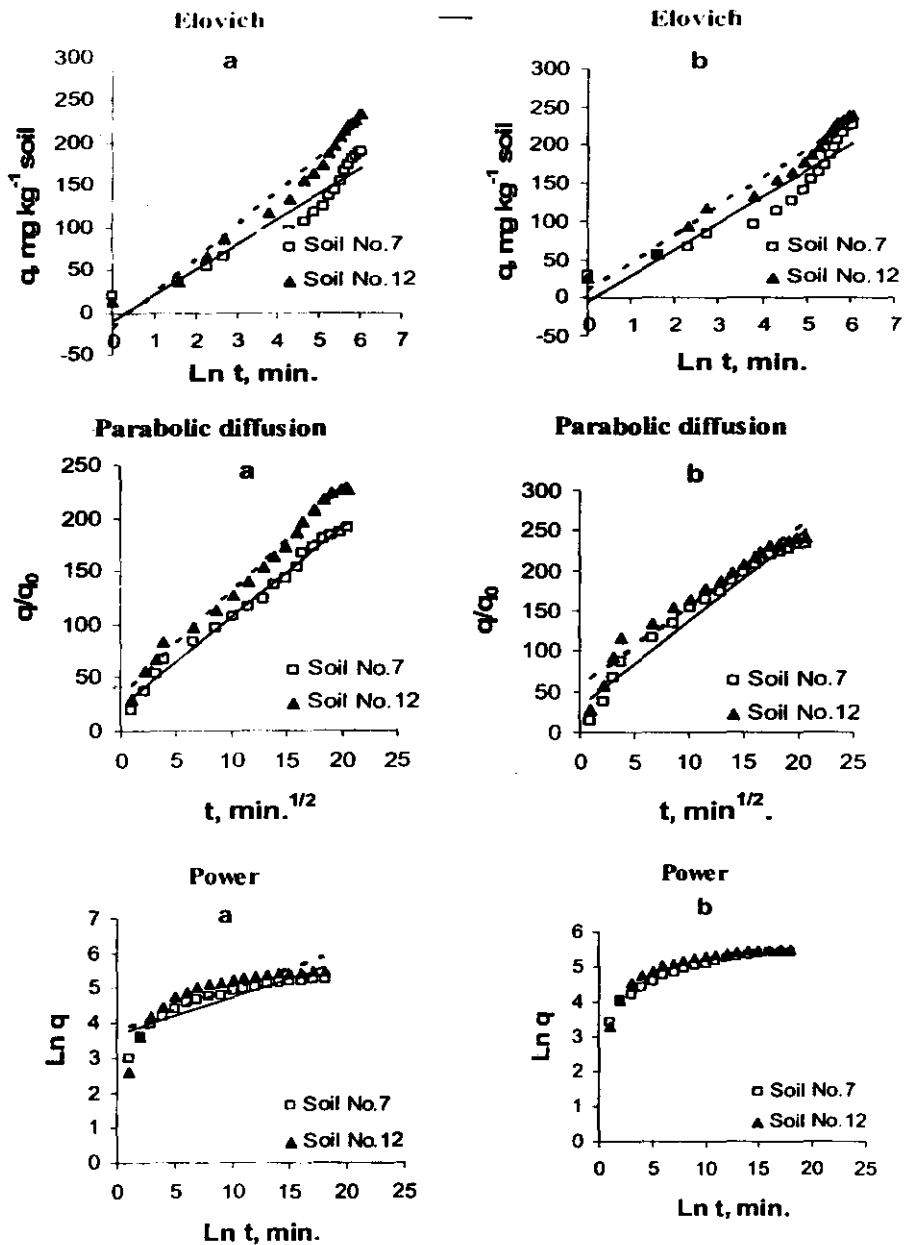


Fig. 3. Relationship between the time and released K with 0.01 M CaCl₂ (a) or 0.01M Oxalic acid (b) solution as described by three mathematical models in the Egyptian soils.

Note: q : The cumulative K released. and q_0 : The maximum K released.

حركية تحرر البوتاسيوم في بعض الاراضي الجيرية الليبية والمصرية

ماهر جورجى نسيم^١ ، ماجدة أبوالمجد حسين^١ ، حسين أحمد زيد^١

كمال عبدالسلام عبدالقادر^٢

١- قسم الأراضي والكيمياء الزراعية-كلية الزراعة (سبأيا باشا) جامعة السكندرية

٢- قسم التربة والمياه - كلية الزراعة - جامعة عمر المختار - البيضاء- ليبيا

الهدف من هذه الدراسة هو بحث حالة وحركية تحرر البوتاسيوم في ١٢ عينة تربة جيرية من ليبيا

(٦ عينات) ومصر (٦ عينات) .

ولقد تم إستخلاص هذه العينات لتقدير صور البوتاسيوم المختلفة في التربة . وكانت متوسط كمية

هذه الصور في ترتيب متزايد هي : البوتاسيوم الذائب (٠,٧٥ ، ٠,٦١ مجم / كجم تربة) ، البوتاسيوم

المتبادل (٣,٢٤ ، ٢٨,٨١ مجم / كجم تربة) ، البوتاسيوم غير المتبادل (٣٣٧,٦ ، ٣١١,٩٢ مجم /

كجم تربة) ، البوتاسيوم المعدنى (٤٢٣٩,٤ ، ٢٥١٦,٥٤ مجم / كجم تربة) ، والبوتاسيوم الكلى (

٤٦١٠,٠٠ ، ٢٨٥٦,٦٧) للأراضي الليبية والمصرية على التوالي.

ولقد تم قياس معدل التحرر للبوتاسيوم في هذه الأراضي والذي أمكن التعبير عنه بقيم حسابية . وقد تم

إستخلاص البوتاسيوم بإستخدام محاليل ٠,٠١ مول كلوريد الكالسيوم أو ٠,٠١ مول حمض الأوكساليك

لفترات زمنية تراوحت بين ١ - ٤٢٥ دقيقة . ثم تم توقيع العلاقة بين الكميات المختلفة والزمن فتكونت

منحنيات تتكون من جزئين ، تعبر عن معدلين لتحرر البوتاسيوم من التربة . فالجزء الأول يعبر عن

البوتاسيوم الذائب والمتبادل . أما الجزء الأخر يعبر عن تحرر البوتاسيوم غير المتبادل في الغالب وهو

البوتاسيوم بطئ الإمتصاص. ولقد تم وصف هذه العلاقة بإستخدام ثلاثة نماذج رياضية هي :

Elovich eqation (iii) Power function (ii) Parabolic diffusion (i)

ولقد وجد أن معادلة **Elovich** و **Parabolic** تستطيع أن تصف حركة تحرر البوتاسيوم في كلا من الأراضي الليبية والمصرية على الترتيب بصورة مرضية كما وجد أيضاً أن معادلة **Elovich** تستطيع وصف هذه العلاقة في الأراضي المصرية أيضاً مما يشير إلى إمكانية تحرر البوتاسيوم غير متبادل و الذي يمكن أن يستفيد منه النبات حيث يتوفر البوتاسيوم غير متبادل في هذه الأراضي.