Release Kinetics of Silicon in Some Egyptian Soils

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ABSTRACT: The objective of this study was proposed to evaluate the kinetics of silicon (Si)released insome Egyptian soils (sandy, calcareous and alluvial). The processes involved in the release of Si from soils during the extraction with 0.01F calcium chloride ($CaCl_2$) were investigated. A considerable amount of Si was released from most of the tested soil samples during the first hours of extraction and continued steadily until the end of the experiment (144 hrs). On average the total Si released for each soil group was 34.80, 93.78 and 62.35 mg kg^{-1} soil in sandy, calcareous and alluvial soils respectively. The released Si was the least in sandy soils. Four mathematical models (parabolic diffusion, power function, and Elovich equation) were used to describe cumulative Si release. The Elovich equation proved that the Si release kinetics was satisfactory in the Egyptian soils.

Key words: silicon ,release , kinetics ,Egyptian soils, Si release.

INTRODUCTION

Silicon is an element beneficial for plant growth and its importance in agriculture is well recognized. The Si experiments indicated that silicon affects plant growth and crop quality, stimulates photosynthesis, reduces transpiration rate, and enhances plant resistance to a series of both a biotic and biotic stresses such as water and chemical stresses, nutrient imbalances, metal toxicities, diseases and pests problems (Epstein, 1994; Ma and Takahashi, 2002;Flore *et al.*,2012).

The release of soluble Si from soils has been much studied. The concentration of Si in soil solution seems to be controlled more by chemical kinetics than by thermodynamics (Hallmark *et al.*, 1982) and apparently had no relationship to the total in soil. Komdorfer *et al.*(1999) noted that the Si content in plants is greater higher as the soluble Si is increased in soil solution. According to Drees *et al.* (1989) the dissolution kinetics of soil Si are influenced not only by nature of Si polymorphs but also by a many of soil factors such as organic matter, redox potential, metallic ions, phyllosilicate, sesquioxide, surface area, surface coatings, and overall soil solution dynamics. As particle size decreases or surface area increases, the dissolution rate of Si minerals increases (Huang and Vogler, 1972). Gibson (1994) has determined the kinetics of Si from soil during the first hour of extraction with 0.01 F $CaCl_2$, and continued steady for 144 hours.

Several reports were, however, proposed to describe the extraction of soils with strong acids and bases, or other extractants. No attempt was made to understand the kinetics of Si release in Egyptian soils. This paper the release of Si from soil during extraction with 0.01F $CaCl_2$. This extractant, which is being designed to reflect the ionic strength and pH of soil solution, is commonly used in determining a number of soil characteristics. Release of Si was studied in someselected soil samples to cover three groups of soil in Egypt.

MATERIALS AND METHODS

Nine surface soil samples (0-30 cm) were collected from fields representing areas of different, soil types. Egyptian soils were grouped on the basis of geographical location and mode of formation (Kishk*et al*., 1973) into three main groups namely, Nile alluvial, Oolitic limestone and Desertic soils. The soil samples were air-dried; sieved (2 mm mesh) and the physical and chemical properties of these soils were carried out according to the methods described by Page *et al.* (1982) and presented in Table 1.

Table (1). Some properties of the tested soils

Soil no.	Location	pH (1:1)	EC dS/m (1:1)	O.M %	$CaCO_3$ %	Total Si g/kg	Particle size distribution			Texture
							Clay %	Silt %	Sand %	
					Sandy soils					
1	El bostan	7.47	2.04	0.03	3.72	436.3	9	3	88	Loamy Sand
2	El bostan	7.62	1.02	0.07	3.37	440.6	8	3	89	Loamy Sand
3	El bostan	7.70	0.48	0.07	2.11	422.1	8	2	90	Loamy Sand
					Calcareous soils					
4	Maryout	8.17	4.07	0.71	39.65	201.2	26	30	44	loam
5	Borg El Arab	8.25	1.89	0.73	32.84	188.6	28	30	42	Clay loam
6	Bangar ElSokar	7.86	1.88	0.88	28.07	182.4	30	32	38	Clay loam
					Alluvial soils					
7	Abis	8.13	3.76	1.66	20.07	254.2	34	28	38	Clay loam
8	Kaleen	8.15	1.68	0.71	3.23	230.4	32	40	28	Clay loam
9	Kom amada	8.43	1.57	0.56	2.11	276.6	24	28	48	loam

*Calcium carbonate content in soil no.7 is in shells form

The capacity of the soils for silicon release was tested through extraction with 0.01F $CaCl_2$according to Gibson (1994). Experimentally, 4g of each soil sample was transferred with 20 ml of 0.01F$CaCl_2$ solutionto a polyethylene bottle at about 25^oC. The samples were then equilibrated on a reciprocating shaker at a rate of 120 strokes min^{-1} for intervals ranging from 1 to 144 hrs.

At the end of the equilibrated period, the suspensions were filtered and the concentration of Si in the supernatant was measured by the molybdenum blue method of Heffenan (1985).

The kinetics of soil Si released for each treatment was described using the following equations (Sparks, 1995):

-First order, $\ln k_t = a - bt$-Parabolic diffusion,$k_t = a + b\, t^{1/2}$
-Power function,$\ln k_t = \ln a - b \ln t$-Elovich equation,$k_t = a + b \ln t$
Where k_t is the cumulative Si released at time t,a and b are constants, and t is time(hr).These mathematical models were tested by least square-regression analysis to determine which equation best describes the Si release from the soils. Standard errors of estimate (SE) were calculated by:

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

Where k_t and k_t* represent the measured and predicted silicon released, respectively, and n is the number of data points evaluated.

RESULTS AND DISCUSSION

Cumulative released silicon

The cumulative silicon released by extraction with 0.01 F $CaCl_2$ was plotted against extraction time in sandy soils (Fig.1), calcareous soils (Fig.2), and alluvial soils (Fig.3) the results have shown that the amount of released Si was increased with increasing time of extraction. The trend in cumulative Si release pattern was almost similar for the three soil groups.The patterns of the curves indicate that there are two stages of release. The first stage, particularly, at the beginning of the extraction is characterized by extraction of soluble and weakly bonded Si, while the latter stage is characterized by release of strongly bondedSi. The rate of increase was sharply decreased after the first few hours of the experiments, and became essentially linear after about 24 hours. The variations in the total amount of released Si from different soil groups (Table 2) could be attributed to many factors such as particle size and type of Si-bearing minerals and soil environment (Drees*et al.*, 1989). However, the total amount of Si released into 0.01M $CaCl_2$ was the higher in the calcareous soils. The average total Si released for each soil group were 34.80, 93.78 and 62.35 mg kg^{-1} soil in sandy, calcareous and alluvial soils respectively (Table 2) anddid not appewr direct relationship to the total in the soil. Comparatively high soluble Si in the calcareous soils may have been due to less leaching.

The soluble Si was presumably present as gels or poorly adsorbed species on the surfaces of the soil particles. The lack of a significant fraction of such material in the sandy soils suggested that most of it, if ever present, had been removed by dissolution and leaching. The soils with higher soluble Si were those with finer particle size, for which higher water retention and lower leaching rates are being expected. This would suggest that water retention, associated withthe slow dissolution of crystalline material and reduced leaching (as against evaporation of the water in *situ),* played an important role in determining the level of soluble Si. The dissolution curves for Si were regular and smooth and behaved similarly for all the samples. This would indicate that the same processes were occurring in all samples, and that this process was not affected by other chemistry (e.g. changes in pH and other chemical parameters) in solution. The rate of dissolution after the first hours, after the initial release of easily soluble material, probably reflected the surface chemistry and mineralogy of the soil particles.

The results of this study indicate that the amounts of Si extracted from soil by $CaCl_2$ are very dependent on the period of the extraction. Measuring Si after an arbitrary time period will give some indication of the extracting easily soluble Si.Due to the differing chemical properties of various soil samples, there is no easy method to determine extractable Si. All extractive methods are empirical, and this study highlights yet the need for further studies be kept in mind when discussing soil chemistry.

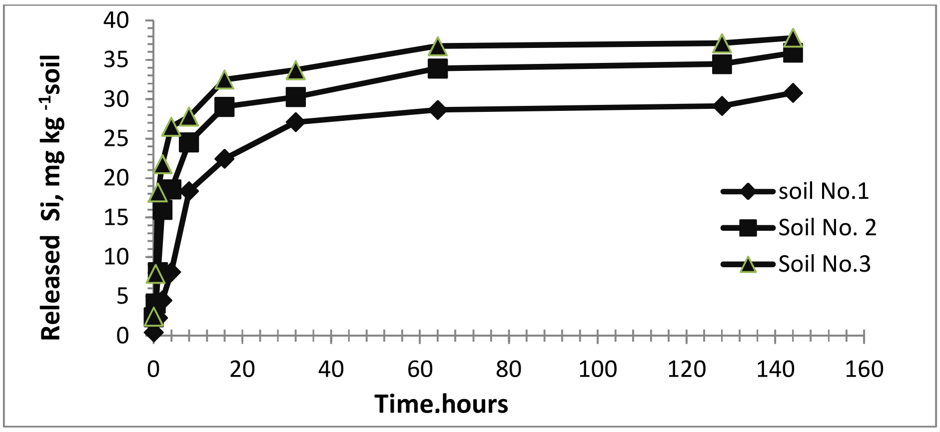
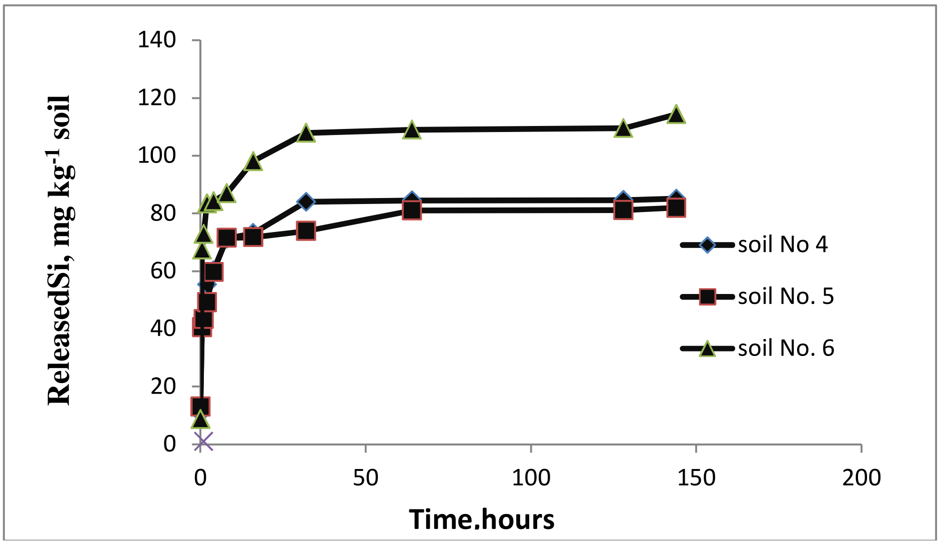
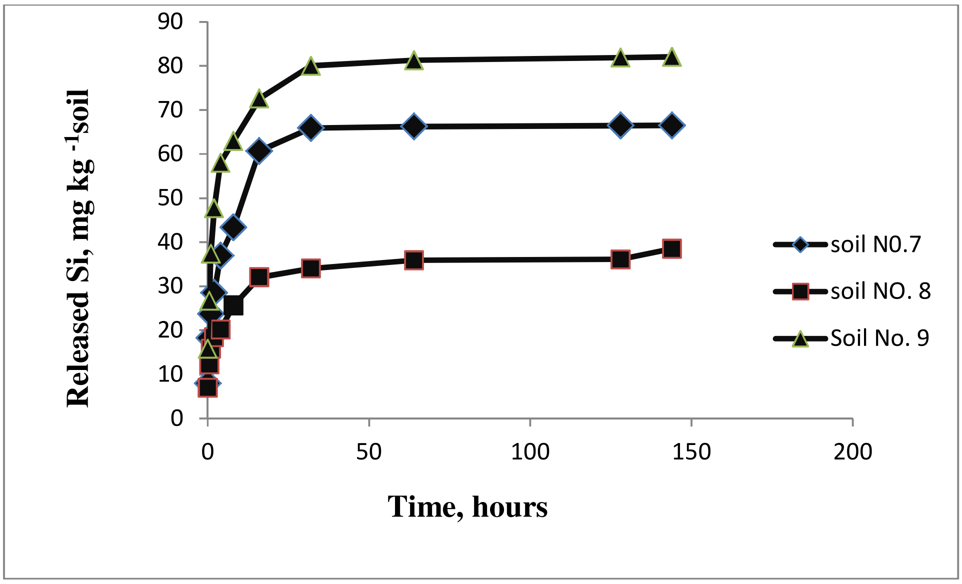


Figure (1). Cumulative Si release with time in the sandy soils



Figure(2).Cumulative Si release with time in the calcareous soils



Figure(3). Cumulative Si release with time in the alluvial soils

Description of Si release by kinetic models

Four mathematical models: first order, parabolic diffusion, Elovich, and power function equations were tested to describe the kinetics of Si release for the soils of the three groups and are illustratedin Figures4, 5 and 6.Table 2 gives the average determination coefficients (R^2), estimated standard errors (SE) and parameters of the tested models (a and b). Based on the highest value of R^2 and the lowest value of standard error (SE) for the tested soils, Elovich equation satisfactorily describes the reaction rates of Si release. However, Power function could also describe the release of Si as shown by higher R^2 and lower SE values in the alluvial soils.

The constants a and b of each model represent the intercept and the slope of the linear curves resulting from plotting the released Si vs. time (Figs,4,5and 6). The constant b mirrors the release rate of Si (Table 2) and the less in sandy soils, indicating the less soil inability to meet the Si demand by the crop than the calcareous or alluvial soils.

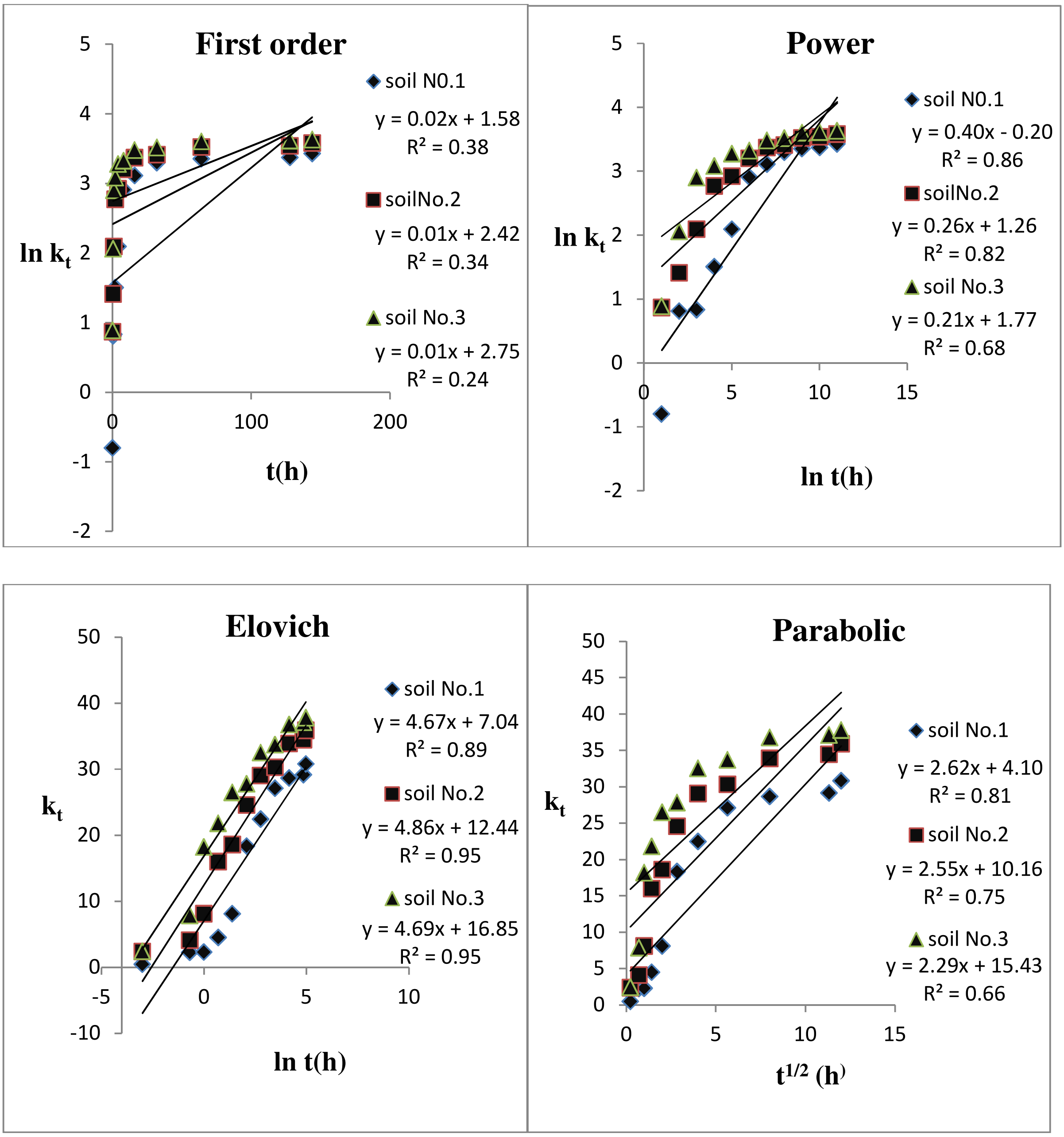


Figure (4). Relationship between the time and released Si with 0.01 F $CaCl_2$solution as described by four mathematical models in the sandy soils.

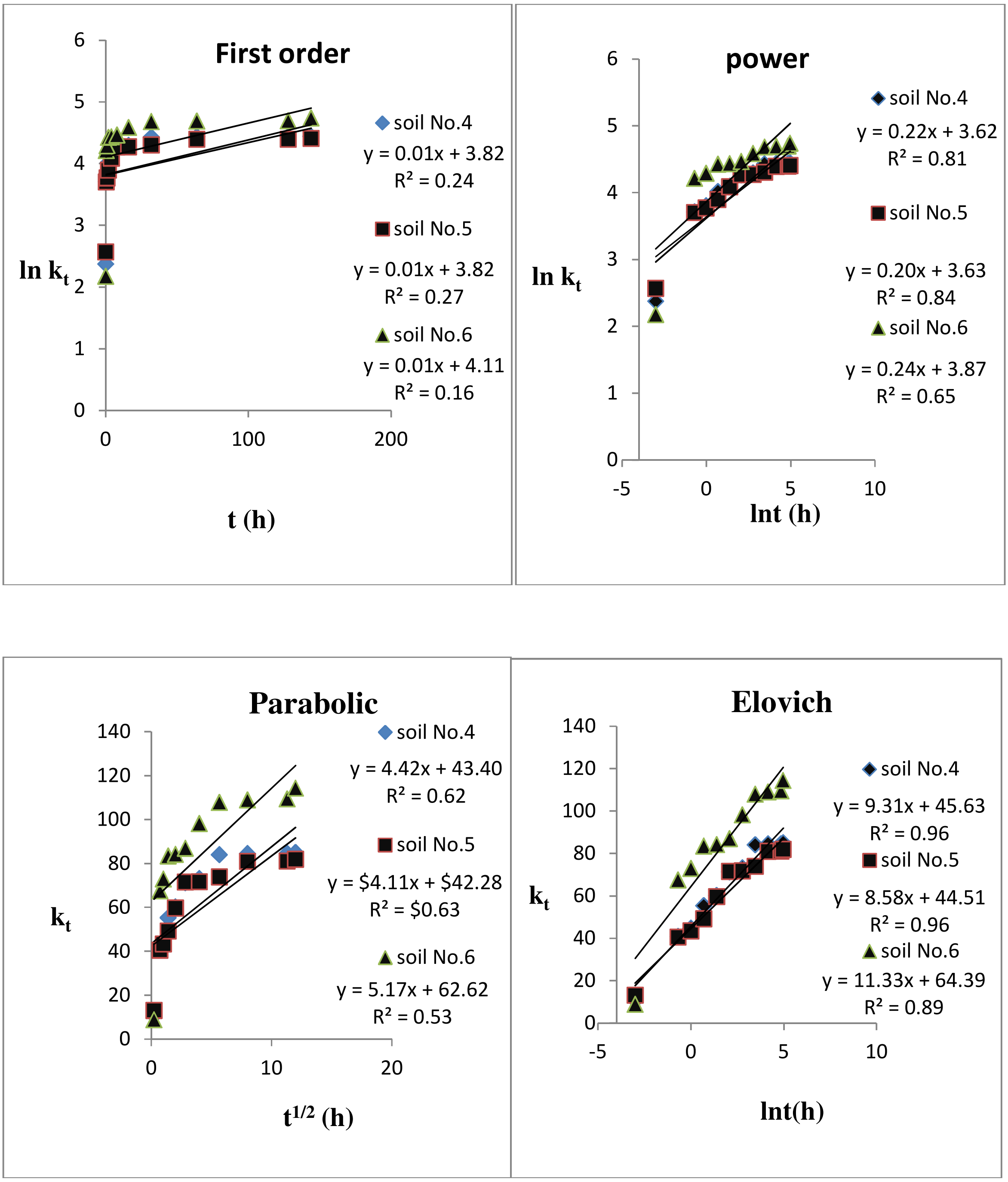


Figure (5). Relationship between the time and released Si with 0.01 F $CaCl_2$solution as described by four mathematical models in the calcareous soils.

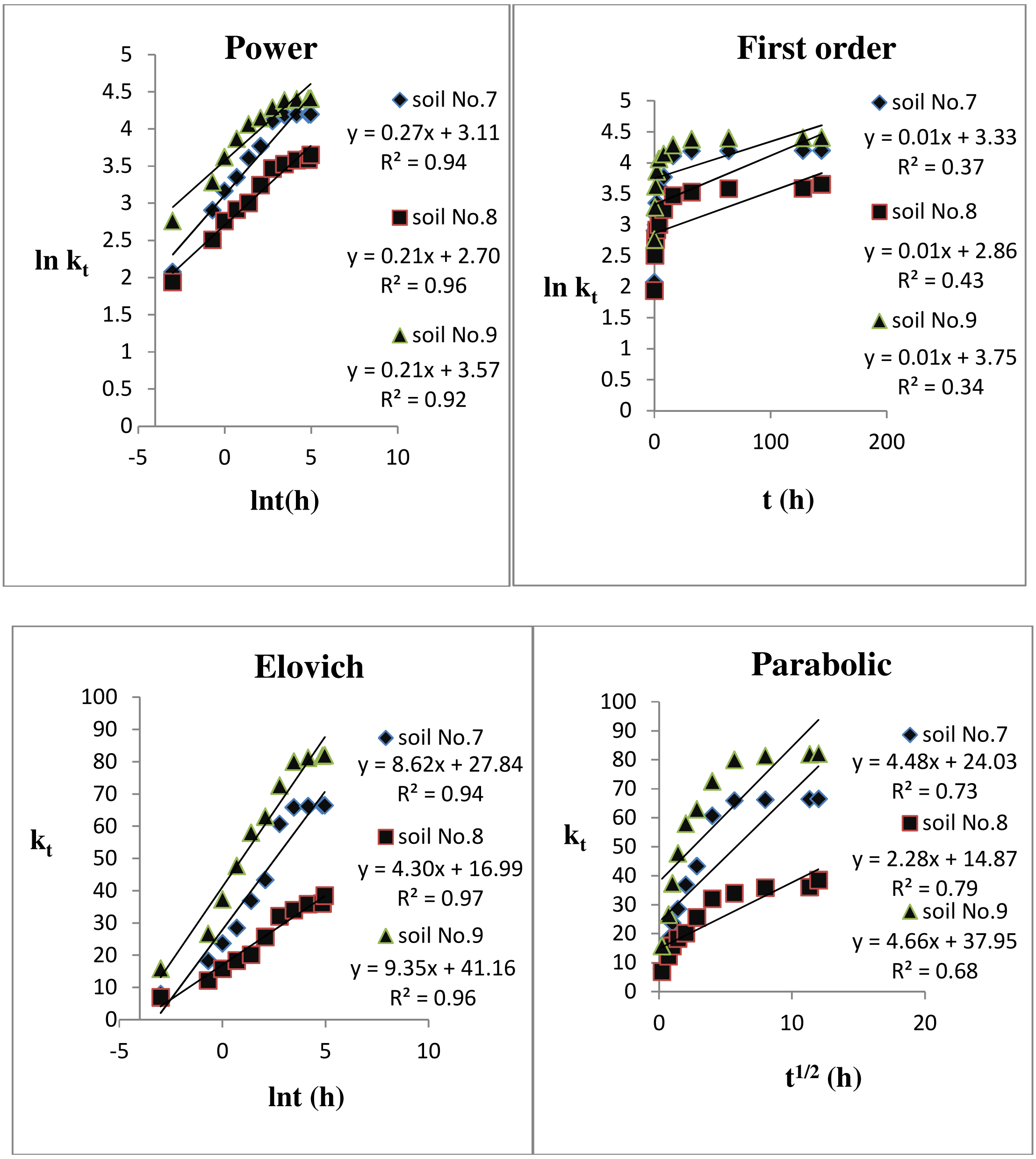


Figure (6). Relationship between the time and released Si with 0.01 F $CaCl_2$solution as described by four mathematical models in the alluvial soils.

Table (2) . Average of determination coefficients (R^2), standard error (SE) and parameters of the models used to describe Si release in the studied soils

Kinetic model	R^2	SE	a	b
Sandy soils				
First order $\ln k_t = a - bt$	0.321	11.780	2.247	0.012
Power $\ln k_t = \ln a + b\ln t$	0.884	8.3733	1.909	0.403
Elovich $k_t = a + b\ln t$	0.929	4.605	12.110	4.741
Parabolic $k_t = a + bt^{1/2}$	0.739	6.568	9.896	2.491
Calcareous soils				
First order $\ln K_t = a - bt$	0.334	53.180	2.827	0.016
Power $\ln k_t = \ln a + b\ln t$	0.765	17.507	3.706	0.217
Elovich $k_t = a + b\ln t$	0.937	6.725	51.510	9.740
Parabolic $k_t = a + bt^{1/2}$	0.597	16.990	49.430	4.566
Alluvial soils				
First order $\ln k_t = a - bt$	0.378	16.288	3.313	0.007
Power $\ln k_t = \ln a + b\ln t$	0.941	7.9141	3.129	0.230
Elovich $k_t = a + b\ln t$	0.955	4.299	28.660	7.422
Parabolic $k_t = a + bt^{1/2}$	0.734	10.529	25.616	3.806

The b values are known to correlate well with crop Si released from soil and can be used as an index of Si release rates. When plant uptake does not positively correlate with the b value, this may represent the soil's inability to meet the Si demand by the crop. On the other hand, a high positive correlation could used as an indication of adequate Si release to meet the crop Si needs. Out of the four models used to describe Si release in the 9 samples of soils, the results proved that the Elovich equation is considered the best fit (R^2 and SE) and displayed the b values of 4.71, 9.74 and 7.422 mg kg^{-1} $h^{-1}$for sandy, calcareous and alluvial soils, respectively using 0.01F $CaCl_2$ for Si extraction. Generally, the Elovich model had the best fit the fitting of the data indicated diffusion control, in all soils,expressing by an initial fast rate followed by a slower rate. Information obtained from mathematical models are beneficial to explain the release mechanism(s) and estimate the Si supplying power of soils. The results provide a basis for the following observations:

1) The Elovich equation adequately described the Si release kinetics of the tested soils.
2) The Si release rates are the least in sandy soils in comparison to the calcareous or alluvial soils.
3) A thorough study is being conductive to evaluate Si potential using quantity and intensity factors and hence, ranking the soils on the basis of their Si supplying power to maintain different crops production especially for crops that require large amounts of Si for growth(rice andsugarcane).

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الملخص العربي

حركية تحرر السليكون فى بعض الأراضي المصريه

حنان اسماعيل – ماهر جورجى نسيم – ماجدة أبوالمجد حسين

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الهدف من هذه الدراسة هو بحث حركية تحرر السليكون فى أراضى مصريه (رملية وجيرية ورسوبية) . وتتضمن العمليه تحرر السليكون من هذه الأراضى من خلال عملية استخلاص باستخدام محلول كلوريدالكالسيوم ٠.٠١ فورمال. ولقد تم تحرر كميه معقولة من عينات التربة المختبره خلال الساعات الأولى من الاستخلاص والذى استمر بصورة مطرده حتنهاية التجربة(١٤٤ ساعة). ولقد كان متوسط كمية السليكون المحرره من كل نوع تربة هو ٣٤.٧٨ و ٩٣.٧٨ و٦٢.٣٥ ملليجرام لكل كيلو جرام تربة فى الأراضى الرمليه والجيريه والرسوبيه على الترتيب. وكان السليكون المحرر من الأراضى الرمليه هو الأقل. ولقد تم وصف السليكون التراكمى المحرر باستخدام أربعة نماذج رياضية ولقد وجد أن معادلة Elovich تسستطيع أن تصف حركية تحرر السليكون فى كل من الأراضى الرملية والجيرية والرسوبيه بصورة مرضيه.