

**KINETICS OF POTASSIUM DESORPTION FROM ENTISOL,
VERTISOL AND MOLLISOL USING MISCIBLE DISPLACEMENT
TECHNIQUE IN SULAIMANI GOVERNORATE.**

Ghafoor A. Mam Rasul
Univ. of Sulaimani / College of Agric.

Mohamad A. J. Al-Obaidi
Univ. of Mosul / College of

Agric.

Soil and Water Sci. Dept.
Dept.

Soil and Water Sci.

ABSTRACT

Kinetics of desorption were conducted on soil samples previously examined for adsorption characteristics from the surface horizon of seven soils of Sulaimani governorate in Kurdistan region of Iraq by using miscible displacement technique . The soil samples were leached with 0.001M CaCl₂. The solution of CaCl₂ was passed through the soil at flow velocities of 1ml min⁻¹. Ten- milliliter aliquots were collected until K was not detected in the leachate.

Potassium desorption conformed to Elovich and Parabolic diffusion equations kinetics. Potassium desorption as plotted by Elovich and parabolic diffusion equations in Ca- saturated soils was rapid at first and leveled off with the time indicating more difficult desorption reaction. Apparent desorption rate coefficient (K_d) for Elovich equation ranged from 0.0604 to 0.0441 cmol kg⁻¹ min⁻¹, while the rate coefficient K desorption (K_d) according to parabolic diffusion equation ranged from 0.0188 to 0.0476 cmol kg⁻¹ min^{-1/2}.

INTRODUCTION

Equilibrium reactions existing between solution and exchange phases of soil K profoundly influence K chemistry. The rate and direction of these reactions determine whether applied K will be leached into lower soil horizons, adsorbed by plants, converted into unavailable forms or released into available forms. Knowledge of the reaction rates between solution and exchangeable phases of soil K is necessary in order to predict the rate of added K fertilizer in soils and to properly make K fertilizer recommendation (Sparkes *et al.*, 1980). Numerous experiments have been done on the potassium exchange equilibria with different cation systems on different soils, but information is inadequate on the kinetics of K desorption on complex soil system (Sparkes *et al.*, 1980; Choudhary and Prasad, 1997). The kinetics of K desorption in heterogeneous soil systems was shown to conform to first order kinetics and to the parabolic diffusion law (Sivasubramanim and Talibudeen, 1972). Elovich equation was superior to the first order rate approach, since the former method tended to combine simultaneous first order reactions into one linear slop. Jardine and Sparks (1984) reported a rapid kinetics of exchange on external planar sites, slow kinetics of exchange on interlattice exchange sites and intermediate kinetics of exchange on interlattice edge sites. Sparks *et al.* (1980) investigated the kinetics of K exchange on soils and clay minerals. These studies have shown that the rate of exchange between solution and exchangeable K forms is

diffusion controlled. Talibudeen *et al.* (1978) observed that the rate of release of soil K was linearly proportional to the square root of time whereas Mortland (1958) found that the release rate of K from biotite was of the

Received 3/5/2010 accepted 4/10/2010

first order using a batch technique and a zero order with a miscible displacement technique. On the basis of least square regression analysis, Dhillon and Dhillon (1990) observed that the parabolic diffusion equation could explain better the kinetics of non- exchangeable K release. Recently, Hundal and Pasricha (1993), however, observed two simultaneous first order equations indicating both a rapid and a slow reaction rate.

The objectives of the present investigation were (1) to determine the rate of K desorption between exchangeable and solution phases in soil samples previously examined for K adsorption characteristics. The magnitude and rate of K desorption were determined using a miscible displacement technique. (2) to determine apparent K desorption rate coefficients (K_d) and reaction order.

MATERIALS AND METHODS

Seven soil samples belonging to agriculturally important soils were taken from agricultural regions in Sulaimani governorate in Kurdistan region, Iraq to study of kinetics of K desorption. The soil particle size distribution was determined by the pipette method (Gee and Bauder, 1986). Organic matter (OM) was determined by dichromate oxidation (Walkley and Black) procedure (Nelson and Sommers, 1986). pH was measured in a saturated paste using a combination electrode (Robbins and Wiegand, 1990); Electrical conductivity (EC_e) was measured for the soil saturation extract with EC-meter, model ((WTW82362 Weilheim, Germany); soluble CO_3 , HCO_3 , Cl and Ca + Mg by titration methods (Page *et al.*, 1982); Na and K by flame photometer; Cation exchange capacity (CEC) was obtained by saturation with 1M ammonium acetate (NH_4OAc) at pH 8.1 as an extraction solution (Polemio and Roades, 1977). Total calcium carbonate ($CaCO_3$) in the soil, expressed as the calcium carbonate equivalent (CCE) was determined by a rapid titration method (Rayment and Higginson, 1992). The active lime or active $CaCO_3$ equivalent (ACCE), which is fine particle- size calcite, was determined by the 0.5 M NH_4 -oxalate method (Drouineau, 1942). Physical and chemical characteristics of the soil samples are given in table (1, 2).

Table (1): some physical properties of investigated soils.

| Location | Depth cm | Soil order | PSD $g\ kg^{-1}$ | | | Texture Class |
|------------|-------------|------------|------------------|-------|-------|------------------|
| | | | Sand | Silt | Clay | |
| Bazyan | 0-10 | Entisols | 58.6 | 574.5 | 366.9 | SiCL |
| Arbat | 0-15 | Entisols | 62.9 | 543.9 | 393.2 | SiCL |
| Bakrajow | 0-12 | Vertisols | 69.8 | 464.4 | 465.8 | SiC |
| Qlyasan | 0-12 | Vertisols | 99.6 | 430.1 | 470.3 | SiC |
| Kanypanka | 0-25 | Mollisols | 33.9 | 508.0 | 458.1 | SiC |
| Said Sadiq | 0-10 | Mollisols | 174.5 | 377.0 | 448.5 | C |
| Serwa | 0-18 | Mollisols | 13.14 | 443.5 | 543.3 | SiC |

Kinetics of Desorption Studies: The miscible displacement technique used for desorption studies as described by (Sparks and Rechcigl, 1982; Chaudhary

and Prasad, 1999). A duplicate 1.00 gm of soil samples previously examined for K adsorption characteristics in to 47mm Nucleopore filter- column. The soil samples were leached with 0.01 M CaCl₂. The solution of CaCl₂ was passed through the soil at flow velocities of 1ml min⁻¹. Ten- milliliter aliquots were collected until K was not detected in the leachate. Potassium in the leachate was determined by flame photometer and K desorbed (cmol kg⁻¹soil) was calculated.

Table (2): some chemical properties of investigated soils

| Soil properties | | Locations | | | | | | |
|--|--------------------------------|-----------|-------|----------|---------|-----------|------------|--------|
| | | Bazyan | Arbat | Bakrajow | Qlyasan | Kanypanka | Said Sadiq | Serwa |
| pH | | 7.83 | 8.18 | 7.54 | 7.90 | 7.46 | 7.80 | 7.65 |
| EC _e (dS m ⁻¹) | | 0.52 | 0.38 | 0.66 | 0.52 | 0.27 | 0.42 | 0.33 |
| CEC (cmol _c kg ⁻¹) | | 46.18 | 51.56 | 48.94 | 50.25 | 55.33 | 50.74 | 50.84 |
| O. M. (g kg ⁻¹) | | 31.70 | 30.50 | 24.40 | 33.70 | 26.50 | 29.80 | 23.20 |
| CaCO ₃ equ. (g kg ⁻¹) | Total | 197.70 | 33.80 | 325.50 | 389.40 | 225.50 | 81.60 | 150.00 |
| | active | 70.00 | 20.00 | 110.00 | 150.00 | 100.00 | 10.00 | 65.00 |
| Soluble ions (mmol L ⁻¹) | Ca ²⁺ | 2.11 | 1.79 | 2.62 | 2.38 | 1.16 | 1.67 | 1.47 |
| | Mg ²⁺ | 0.91 | 0.49 | 0.70 | 0.48 | 0.34 | 0.58 | 0.32 |
| | Na ⁺ | 0.47 | 0.41 | 0.50 | 0.41 | 0.42 | 0.43 | 0.44 |
| | K ⁺ | 0.11 | 0.01 | 0.11 | 0.11 | 0.08 | 0.13 | 0.01 |
| | HCO ₃ ⁻¹ | 5.08 | 4.39 | 4.16 | 3.76 | 2.75 | 3.63 | 3.34 |
| | Cl ⁻¹ | 0.78 | 0.30 | 1.10 | 0.86 | 0.42 | 0.88 | 0.66 |
| | SO ₄ ²⁻ | 0.87 | 0.79 | 0.87 | 0.88 | 0.93 | 0.87 | 0.85 |

Potassium desorption (cmol kg⁻¹soil) with time was fitted employing different kinetic equations, namely zero order, first order, Elovich, parabolic diffusion, and power function equations:

Zero order equation: $C_t = C_o - Kt$

First order equation: $\ln(C_t/C_o) = K_d t$

Where:

K_d = desorption rate coefficient of potassium

C_t = amount of desorbed potassium at time t (cmol kg⁻¹ soil)

C_o = amount of desorbed potassium at equilibrium (cmol kg⁻¹ soil)

t = time in hours

The value of desorption rate coefficient (K_d) were calculated from the slope of linear relationship between $\log (C_t/C_o)$ vs. t .

Elovich equation : $C_t = 1/K \ln (C_o K) - 1/K \ln t$

Plotting C_t versus the term of the duration of the extraction ($\ln t$) the Elovich equation will be a straight line with the slop (1/K) and logarithmic intercept (1/Kln(C_oK)), the slop of straight line was expressed for the rate coefficient of desorption of K.

Parabolic equation: $C_t = C_o + K_d t^{1/2}$

Where, ' C_t ' is the amount of K desorbed at time ' t ', ' C_o ' is the amount of desorbed K at equilibrium and ' K_d ' is the overall diffusion coefficient and ' t ' is the time in hours.

Power function equation: $\ln C_t = \ln C_0 + k \ln t$

Where:

C_t = the amount of K desorbed at time t.

The equations used to describe the kinetics of K desorption were evaluated by comparing the linear coefficient of determination (R^2) and the standard error (SE) of the estimate. This SE was calculated according to the equation:

$$SE = [\sum (C_t - C_t^*)^2 / n - 2]^{1/2}$$

Where ' C_t ' and ' C_t^* ' represent the amount of metal measured and calculated at time ' t ' respectively, and ' n ' is the number of measurement points for each equation which were determined by least squares regression analysis (Martin and Sparks, 1983; Havlin *et al.*, 1985).

RESULTS AND DISCUSSION

The results of K desorption by miscible displacement technique are describe according to mathematical kinetic linear equations to choice the best equation depending on highest value of coefficient of determination (R^2) and the lowest value of standard error of estimate (SE) (Sparks, 1992). Table (3) show all equations describe the reaction rate of K desorption in the studied soils as evidenced by the over all highest value of (R^2) and lowest (SE) however potassium desorption in the studied soils conformed to Elovich and parabolic diffusion kinetic equations.

This result is agreed with finding by (Sivasubramanim and Talibudeen, 1972; Dhillon and Dhillon, 1990).

Table (3): Show the value of R^2 and SE for K desorption from the studied soils

| Location | Zero order | | First order | | Elovich | | Parabolic | | Power function | |
|------------|------------|-------|-------------|-------|---------|-------|-----------|-------|----------------|-------|
| | SE | R^2 | SE | R^2 | SE | R^2 | SE | R^2 | SE | R^2 |
| Bazyan | 0.052 | 0.912 | 0.089 | 0.797 | 0.006 | 0.995 | 0.013 | 0.976 | 0.071 | 0.976 |
| Arbat | 0.051 | 0.914 | 0.088 | 0.793 | 0.004 | 0.998 | 0.013 | 0.977 | 0.072 | 0.974 |
| Bakrajow | 0.056 | 0.893 | 0.087 | 0.778 | 0.004 | 0.997 | 0.012 | 0.966 | 0.070 | 0.968 |
| Qlyasan | 0.079 | 0.760 | 0.086 | 0.662 | 0.009 | 0.960 | 0.017 | 0.872 | 0.105 | 0.906 |
| Kaneypanka | 0.025 | 0.966 | 0.099 | 0.842 | 0.017 | 0.979 | 0.021 | 0.997 | 0.056 | 0.991 |
| Said Sadiq | 0.053 | 0.914 | 0.071 | 0.808 | 0.002 | 0.999 | 0.010 | 0.998 | 0.054 | 0.979 |
| Serwan | 0.042 | 0.954 | 0.069 | 0.860 | 0.009 | 0.988 | 0.006 | 0.995 | 0.031 | 0.995 |
| mean | 0.051 | 0.902 | 0.084 | 0.791 | 0.007 | 0.988 | 0.013 | 0.966 | 0.066 | 0.970 |

The rate coefficient of K desorption (K_d) by using miscible displacement to Elovich equation ranged between 0.0604 and 0.1441 $\text{cmol kg}^{-1} \text{min}^{-1}$. In the whole soil, the highest rate constant was for Kaneypanka location soil (Mollisols), and the lowest for Qlyasan location soil (Vertisols) as shown in table (4). While the rate coefficient K desorption (K_d) according to parabolic diffusion equation ranged between 0.0188 and 0.0476 $\text{cmol kg}^{-1} \text{min}^{-1/2}$ the highest rate constant also for Kaneypanka location soil (Mollisols) and the lowest value for Qlyasan location soil (Vertisols). This apparent discrepancy may be attributed to the difference in type and content of minerals in clay fractions.

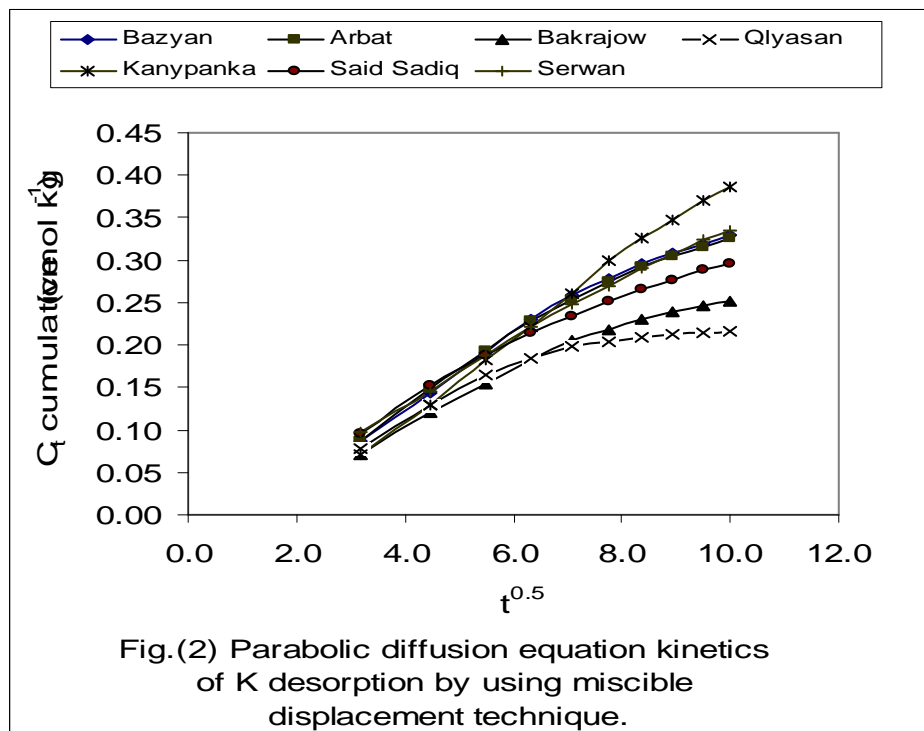
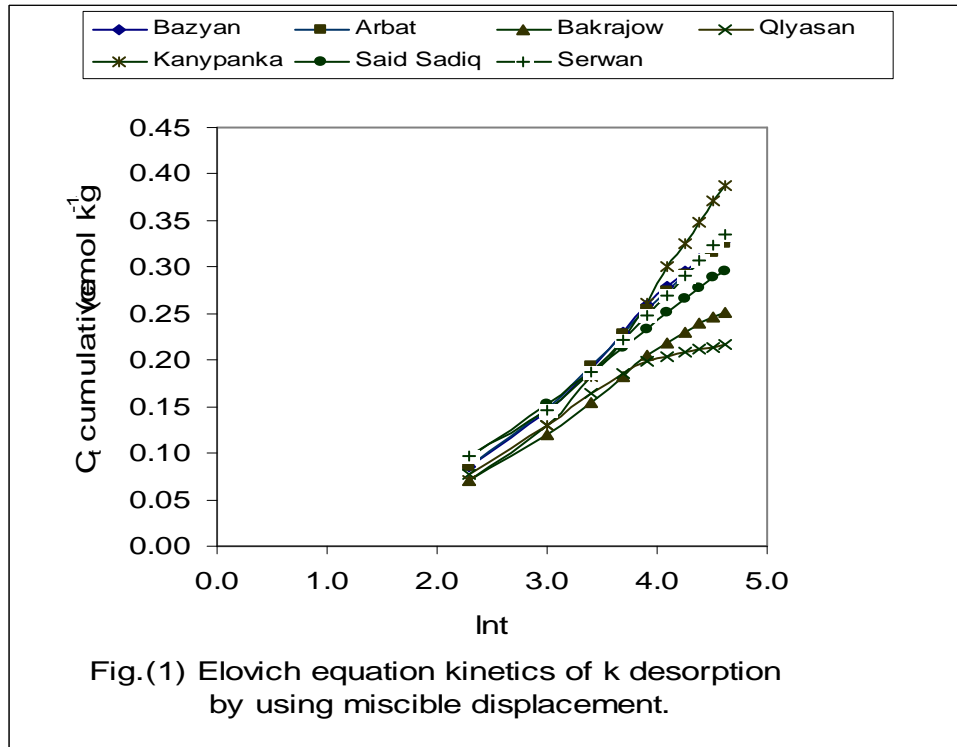
The external planar surface sites and the edge sites desorbed K readily while the desorption of K from interlayer sites involved a slow rate of diffusion

(Sawhney, 1966). The diffusion was the predominant mechanism of K desorption in these soils as illustrated in figures (1 and 2) by the linear relation between the cumulative desorbed K cmol kg^{-1} and $\ln t$ for Elovich equation and between the cumulative desorbed K cmol kg^{-1} and $\text{time}^{1/2}$ for parabolic diffusion equation.

Table (4): Apparent desorption rate coefficients (K_d) calculated at 1.0 ml min^{-1} flow velocity, of studied soils

| Location | Zero order Cmol kg^{-1} min^{-1} | First order min^{-1} | Elovich cmol kg^{-1} min^{-1} | Parabolic cmol kg^{-1} $\text{min}^{-1/2}$ | Power function $\text{cmol kg}^{-1} \text{min}^{-1}$ |
|------------|--|----------------------------------|---|---|---|
| Bazyan | -0.0052 | 0.0055 | 0.1102 | 0.0357 | 0.5778 |
| Arbat | -0.0051 | 0.0054 | 0.1075 | 0.0348 | 0.5663 |
| Bakrajow | -0.0051 | 0.0051 | 0.0816 | 0.0263 | 0.5401 |
| Qlyasan | -0.0044 | 0.0038 | 0.0604 | 0.0188 | 0.4198 |
| Kaneypanka | -0.0042 | 0.0072 | 0.1441 | 0.0476 | 0.7401 |
| Said Sadiq | -0.0054 | 0.0045 | 0.088 | 0.0285 | 0.4744 |
| Serwan | -0.006 | 0.0053 | 0.1072 | 0.0352 | 0.5405 |
| mean | -0.0050 | 0.0052 | 0.0999 | 0.0324 | 0.8418 |

The slopes of the relation of cumulative desorbed K and $\ln t$ for Elovich equation and $\text{time}^{-1/2}$ for parabolic diffusion equation are different for investigated soils. Similar type of relationship between per cent K desorbed and $\text{time}^{1/2}$ was reported by (Sparks *et al.*, 1980; Choudhary and Prasad, 1997) in soils of varying clay content.



حركيات تحرر البوتاسيوم لترب إنتيسول فيرتيسول و موليسول في محافظة السليمانية
 غفور احمد مام رسول
 محمد على جمال العبيدي
 جامعة الموصل / كلية الزراعة
 قسم علوم التربة و المياه
 جامعة السليمانية / كلية الزراعة
 قسم علوم التربة و المياه

الخلاصة

تم دراسة حركيات تحرر البوتاسيوم على عينات مستخدمة سابقاً لإختبار إمتزاز البوتاسيوم لطبقات سطحية لسبع ترب محافظة السليمانية في كردستان العراق بإستخدام تقنية الإزاحة الإمتزاجية الهادئة .

تم غسل عينات بمحلول ٠.٠١ مولاري من كلوريد الكالسيوم و تم تمرير المحلول كلوريد الكالسيوم من خلال التربة و بسرعة ١ ملليتر دقيقة^{-١} و جمعت ١٠ ملليترات من المحلول لحين عدم ظهور البوتاسيوم في الراشح. و تمشى عملية التحرر مع معادلة إلوفيج و معادلة الإنتشار و عملية التحرر كانت سريعة في البداية ثم تعادلت، و كانت معامل سرعة التحرر لمعادلة إلوفيج من ٠.٠٦٠٤ إلى ٠.٠٤٤١ سنتيمول كغم^{-١} دقيقة^{-١} بينما معامل سرعة التحرر حسب معادلة الإنتشار كانت ٠.٠١٨٨ إلى ٠.٠٤٧٦ سنتيمول كغم^{-١} دقيقة^{-١}.

REFERENCES

- Choudhary, K. and B. Parasad(1997). Kinetics of potassium desorption from inceptisols and entisols. Journal. Indian. Soc. Soil. Sci.45:460-464.
- Chaudhary, K. and B. Prasad (1999). Thermodynamics of potassium exchange reaction in entisol and vertisol using a kinetic approach by miscible displacement technique. J. of the Indian Soc. Soil Sci. 2. 221-229.
- Dhillon, S. K. and K. S. Dhillon (1990). Kinetics of release of non-exchangeable potassium by cation-saturated resins from red Alfisols, black vertisols and alluvial (Inceptisols) soils of India. Geoderma 47: 283-300.
- Drouineau, G. (1942). Dosage rapide du calcaire actif du soil: nouvelles donnees surla separation et al nature des fractions calcaires. Ann Agron., 12: 441-450.
- Gee, G. W. and J. W. Bauder (1986). Particle-size analysis. P 383-412. In A. Klute (ed.) Methods of Soil Analysis: Physical and Mineralogy Methods, Part I. Second ed. ASA and SSSA, Madison, WI.
- Havlin, J. L., D. G. Westfall, and S.R. Olsen (1985). Mathematical models for potassium release kinetics in calcareous soils. Soil Sci. Soc. Am. J. 49: 371-376.
- Hundal, L. S. and N. S. Pasricha (1993). Non-exchangeable potassium kinetics in illitic soil profiles. Soil Sci. 156:34-41.
- Jardine, P. M., and D. L. Sparks (1984). Potassium-calcium exchange in a multireactive soil system: I. Kinetics. Soil Sci. Soc. of Am. J. 48: 39-45.
- Martin, H. W. and D. L. Sparks(1983). Kinetics of nonexchangeable potassium release from two coastal plain soils. Soil Sci. Soc. Am. J. 47:883-887.
- Mortland, M. M. (1958). Kinetics of potassium release from biotite. Soil Sci. Soc. of Am. Proc. 22: 503-508.
- Nelson, D. W. and L.E. Sommer(1986).Total carbon, organic carbon and organic matter. In: Page, Methods of Soil Analysis A.L., R.H. Millerand D.R. Krenney, (eds).pp539-579Part.2Agron. 9 SSSA. Madison, W.I. USA.
- Page, A. L., R. H. Miller and D. R. Kenney, (Ed.) (1982). Methods of Soil Analysis. Part 2. Am. Soc. Agric. Pub. Madison, W.I. U S A.
- Polemio, M. and J. D. Roades (1977). Determining cation exchange capacity. A new procedure for calcareous and gypsiferous soils. Soil Sci. Soc. Am. J.
- Rayment, G. E. and F. R. Higginson (1992). Australian Laboratory Handbook of Soil and water Chemical Methods. Inkata Press.

- Robbins, C. W., and C. L. Wiegand (1990). Field and laboratory measurements. In: *Agricultural Salinity Assessment and Management*. K.K. Tanji (ed.) Am. Soc. Civil Eng., New York, pp 201-219.
- Sawhney, B. L. (1966). Kinetics of cesium sorption by clay minerals. *Soil Sci. Soc. Am. Proc.* 30: 565-569.
- Sivasubramaniam, S., and O. Talibudeen (1972). Potassium aluminum exchange in acid soil. I. Kinetics. *J. Soil. Sci.* 23:163-176.
- Sparks, D. L., L. W. Zelazny, and D. C. Martens (1980). Kinetics of potassium desorption in soil using miscible displacement. *Soil Sci. Soc. Am. J.* 44: 1205-1208.
- Sparks, D. L. and J. E. Rechcigl, (1982). Comparison of batch and miscible displacement techniques to describe potassium adsorption kinetics in Delaware soils. *Soil Sci. Soc. Am. J.* 46:875-877.
- Sparks, D. L., 1992. *Kinetics of Soil Chemical Processes*. Academic Press, Inc., (England).
- Talibudeen, O., J. D. Beasley, P. Leone, and N. Rajendran (1978). Assessment of soil potassium reserves available to plant roots. *J. Soil Sci.* 29:207-218.