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Kinetics of Dissolution of Phosphate Rock, Partial Acidulated Phosphate Rock and Tri Super Phosphate in Calcareous Soil.

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ABSTRACT

A study was conducted to evaluate kinetics of phosphorus release from dissolution of phosphate rock (PR), partial acidulated phosphate rock (40%-PAPR) and tri super phosphate (TSP) in calcareous soil by using Batch equilibrium technique for five incubation times. The water soluble phosphorus was measured at end of each incubation times. Six kinetic equations were tested to know which one is the best in description of phosphorus release to soil. The results showed that were gradual increases in the released p from the dissociated 40%-PAPR and TSP. Liberation of p from phosphate rock was so weak with time .The accumulated amount of the released phosphorus at end of incubation time (720h.) was higher in TSP. The phosphorus release curves showed good liberation of phosphorus in PAPR and TSP. The Elovich equation was the best in explaining successfully phosphorus release and the rate of phosphorus release constant (kd) values were 4.38 h^{-1} and 15.11 h^{-1} in PAPR and TSP respectively.

Keywords: Elovich equation, rate of p release constant (Kd), Bach equilibrium technique.

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INTRODUCTION

Chien et al (4) mentioned that the partial dissolution is the first step in utilization by plants of the phosphorus applied to soil as solid phosphate fertilizers and the dissolved phosphorus then may move directly through the soil solution to the plant root surface where it is absorbed. The rate at which the phosphorus appears in solution from phosphate rock is one of the factors that may affect the rate at which phosphorus is transferred to plant root or to soil solid phase(2). Using kinetics concept is the best way to describe sorption and adsorption of phosphorus ion and many other ions such as N, Ca, Mg, and S (6,11,13) .For this purpose ,many kinetic equations are used such as the Zero order, First order, Second order equations which are based on chemical principles , Parabolic and Diffusion equations that are based on physical properties, and Power function and Elovich equations that based on empirical nature(12).

Chien et al (4) got significant increases in the accumulated amount of the released phosphorus with time from different phosphate rocks in acid soils and Elovich equation was the best of six equations that described successfully release of phosphorus .Jabar (7) found that the Elovich equation was the best in describing phosphorus release from phosphate gypsum in the Iraqi calcareous soil, the rate of phosphorus release constant were 4.45 to 44.51 mg p kg^{-1} h^{-1} at zero and 4 mecagram h^{-1} of phosphate gypsum respectively. Study of the kinetic dissolution of some of the solid phosphate fertilizers in soils is needed in order to understand the solubility behavior of phosphate rock, PAPR and TSP used in this research.

MATERIALS AND METHODS

Kinetics of dissolution of some of solid phosphate compounds were studied by using Batch equilibrium Technique. Silty clay loam soil samples collected from College of Agriculture, University of Baghdad field were used and some of the chemical and physical soil properties are shown in Table (1).Ten gram of soil samples were mixed with 100 mg of three phosphate compounds (Akashat phosphate rock(PR),40%-partial acidulated phosphate rock (PAPR)and tri super phosphate (TSP)).Some of the chemical properties of the Iraqi phosphate rock (Akashat) are shown in Table (2).Then they were put in a polyethylene bottles and water was added at a rate enough to maintain soil moisture at 2/3 of the field capacity, aeration was done twice a week and losses of water were replaced using weight method. The samples were incubated at room temperature (21+1)C for five times intervals ,24,72,168,360 and 720 hours. The soluble phosphorus was extracted by using Olsen and Sommer method (9) and measured by spectrophotometer.

Table 1: Some properties of the soil

pH 1:1	7.40
EC e dS.m^{-1}	4.13
Organic matter %	1.36
Olsen available P mgPKg^{-1}	13.75
Avail. N mgKg^{-1}	66.5
Avail. K mgKg^{-1}	485
CEC Cmolc.kg^{-1}	20.20
Carbonate minerals %	16.9
Field capacity %	30
Soil texture	SiCL

Table 2: Some of chemical properties of Ekashat phosphate rock

pH 1:1	7.5
EC e dS.m^{-1}	3.0
K^{+} mgKg^{-1}	728
SO_4^{2-} %	0.246
Ca^{-2} %	29.25
P %	10.22
Mg^{+2} mgKg^{-1}	280
Na^{+} mgKg^{-1}	310

The 40%-PAPR was prepared by adding the needed amount of the concentrated H_2SO_4 to the phosphate rock to reach to 40% of acidulation according to the amount of concentrated H_2SO_4 that used to produce the ordinary super phosphate(OSP)(5).

Six kinetic equations ,Zero order, first order, second order, parabolic diffusion, power function and Elovich were tested to describe phosphorus release from the dissociated phosphate compounds .The mathematical models of the kinetic equations are as follows:

Zero order eq.	(Co-Ct)=Co-Kdt
First order eq.	ln(Co –Ct)=lnCo - Kdt
Second order eq.	1/Ct=1/Co+Kdt
Parabolic diffusion eq.	$Ct/Co=Co+kdt^{0.5}$
Elovich eq.	Ct =Co+Kd lnt
Power function eq.	lnCt=lnCo+Kd lnt

Where Ct is the amount of the released phosphorus at time (t), Co is the total amount of phosphorus that can be released at equilibrium(at zero time) and Kd is the rate constant of the soluble phosphorus release . These mathematical models were tested by least square regression analysis and standard errors (SE) to determine which was the most appropriate for describing the release of the soluble phosphorus from the dissolution of the phosphate compounds.

RESULTS AND DISSCUSSION

Release of soluble phosphorus

Fig.(1) shows the effect of incubation time on the released soluble phosphorus from the dissolution of PR, 40-PAPR and TSP .The amount of the released soluble phosphorus differed with the kind of the used phosphate compounds .The highest amount of the released soluble phosphorus was in TSP followed by PAPR and PR respectively . Three were a gradual increases in solubility of phosphorus in PAPR and TSP with time of the incubation, the high solubility started during the 24 hour of incubation followed by small increases in soluble phosphorus till 306 hour of incubation, the solubility increased considerably from 360 to 760 hours of incubation. The amount of the dissolved phosphorus from PR was so weak through the incubation intervals due to the low solubility (less than 10^{-14}M) of the phosphate rocks (8).

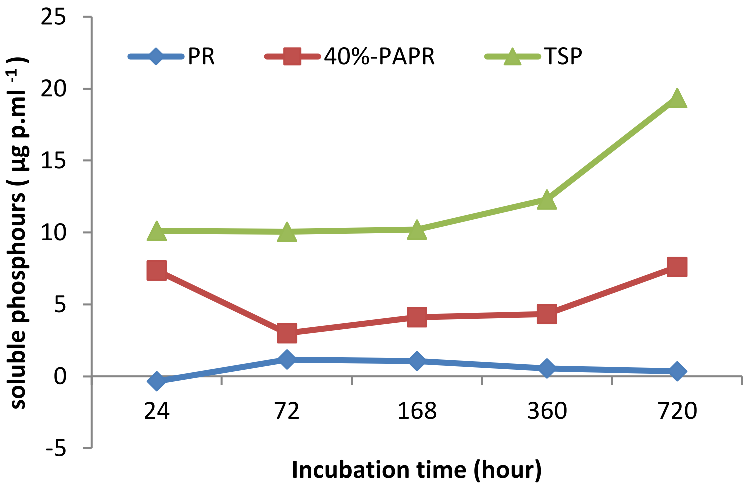

Figure 1: Effect of incubation time on release of soluble phosphorus from the phosphate compounds to soil solution.

Accumulation curves of soluble phosphorus

Fig 2 shows the accumulation curves of soluble phosphorus that released from the 40%-PAPR and TSP with time. The release of p from PAPR and TSP was weak during the beginning of incubation time and then gradually increased with time .The phosphate compounds affected strongly on the amounts of the soluble phosphorus during incubation, the amounts were higher in TSP compared with 40%-PAPR and the slope of the TSP curve (dCt/dt) was 0.014 while it was 0.003 in 40%-PAPR. These results reflect the good and continuous supply of phosphorus from TSP compared with PAPR and PR and agree with finding of Al-Hamadan(1), and also show that acidulation of the phosphate rock increased the solubility of the phosphate rock.

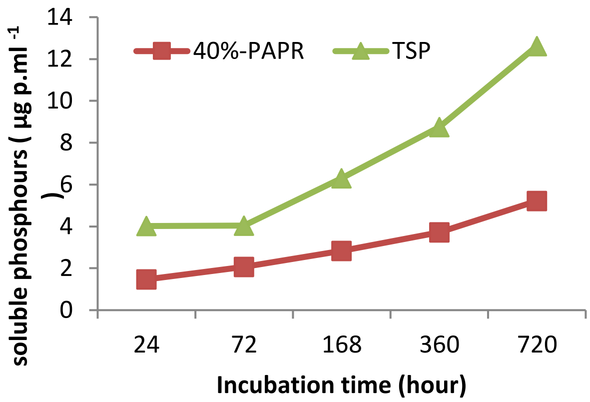

Figure 2: Accumulation curves of soluble P (microgram P ml^{-1}) in 40%-PAPR and TSP.

The Kinetic equations

The kinetic equations were used to describe the relation between the released P and time and the best equation was selected according to the highest correlation coefficient value (r) and lowest standard error value (SE).The Elovich equation described release of P successfully in 40-PAPR and TSP treatments in this study. Successful presentation of Elovich equation for release of soluble phosphorus from PR and some other phosphate compounds has been reported by Chien et al(4) and Sikora et al (10). Chien and Clayton (3) also reported that Elovich equation had good description in kinetic of nutrient release and it was widely used in phosphate rock dissolution and phosphorus release from different solid phosphate compounds. Jabar(7)found that Elovich equation described successfully phosphorus release from phosphate gypsum added to calcareous soil with time of corn growth.

Table(3) and Fig.(3) show the rate constant of soluble phosphorus release of PAPR and TSP (Kd) calculated by using the Elovich equation. The Kd values were 4.375 mg P Kg^{-1}soil h^{-1} in PAPR and 15.11 mgPKg^{-1}soil h^{-1} in TSP. The value of Kd in TSP was greater than PAPR by three times. The kd values of the Elovich model for the dissolution process of the solid phosphate compounds suggesting heterogeneous releases.

Table 3: Rate of phosphorus release constant (kd) values in 40%-PAPR and TSP estimated by using Elovich Equation.

The phosphate compounds	Rate of phosphorus release constant (Kd) Microgram P ml^{-1} h^{-1}	Rate of phosphorus release constant (Kd) mg P Kg $soil^{-1}$ h^{-1}
40%-PAPR	0.875	4.375
TSP	3.022	15.11

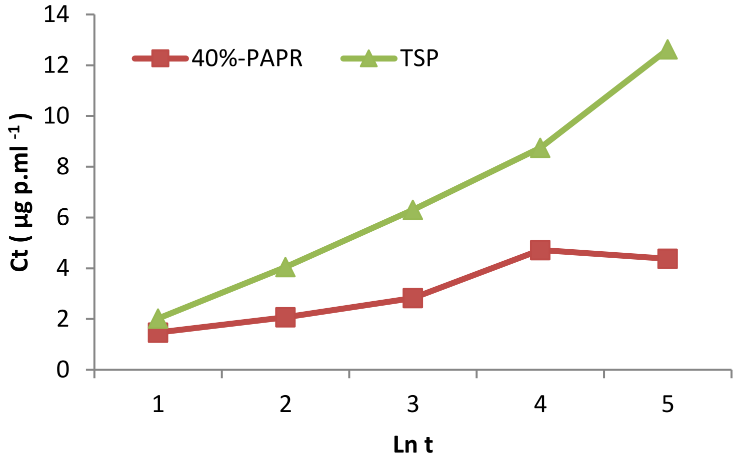

Figure 3: The relation between lnt and Ct in 40%-PAPR and TSP of Elovich equation.

CONCLUSIONS

The amount of the released phosphorus from the used solid compounds differed with time of incubation. The TSP gave good soluble phosphorus supply followed by medium supply in PAPR ,while PR had weak supply. Elovich equation was the best that described release of phosphorus. Differences of kd values reflected differences of solubility of TSP, PAPR and PR and their roles in rate of supplying phosphorus to plants.

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