Original Research Article

INFLUENCE OF ELEMENTAL SULPHUR, OXALIC ACID, AND PHOSPHORIC ACID AS ACIDULATING AGENTS ON PHOSPHOROUS DISSOLUTION FROM ROCK PHOSPHATE

Abstract

Phosphorous is a limiting mineral element in crop productivity due to its less availability and fixed form in the soil. Due to its agricultural benefit, most farmers seek for alternative method to supply phosphorous in sufficient amount in the farming systems. Although the soluble P is relatively expensive for the peasant farms, rock phosphate has proved to be quite efficiency due to availability among the small scale holder. However, rock phosphate is face with insolubility challenges is not readily available in the soils to promote crop growth. Therefore, this study sought to establish the influence of various acidulating agents in dissolution of phosphorus in to rock phosphate. The study was carried out in a laboratory environment in Complete Block Design consisting of the following treatment: control (bare soil); Mijingu Rock Phosphte (MRP) and soil; MRP, soil and oxalic acid; MRP, soil and phosphoric acid; phosphoric acid and soil; MRP, soil and elemental sulphur and replicated three times. The experiment incubation period was 90 days and the phosphorous dissolution rate was measured at interval of 30 days. The result revealed that the treatments had significant ($P \leq 0.05$) influence on the dissolution of the phosphorus from rock phosphate and both soil. Elemental sulphur was superior in increasing the rate of phosphorus dissolution form rock phosphate. At 30 days, elemental sulphur had obtained a total of 37.5ppm phosphorus while the control had the least recording 5.37ppm. A similar trend was observed in both 60 and 90 days. Regression analysis also exhibited positive relationship between the acidulating agents and the phosphorous dissolution rate from the rock phosphate. This was revealed by sulphur that recorded amount of phosphorus 2108.11ppm. Therefore, elemental sulphur can be recommended to be used by in agricultural fields to enhanced solubilisation of rock phosphate and enhance supply of phosphorous.

Key words: soil fertility, fixed phosphate, dissolution agent,

1.0 Introduction

Low soil fertility in crop land is one of the challenging factors towards achieving maximum agricultural productivity. Phosphorus (P) is one of the critical elements that limit plant production, particularly in humid and acid soils [1]. Phosphorus has been reported to have a tremendous effect on proper root formation, establishment and formation for the absorption of mineral salts and water from the soil [2]. The situation is aggravated in smallholder agriculture where use of mineral fertilizers is limited or even non-existent, as peasant farmers, due to their low purchasing capacities, cannot afford high costs of these fertilizers [3]. Rock phosphate (PR) provides an alternative to the expensive soluble P. Unfortunately, use of rock phosphate (PR) to alleviate P deficiency in the soils remains a great challenge due to their low solubility. The PR is water-insoluble but acid-soluble indigenous P source, to be more relevant for these resource-limited farmers, in comparison to the prohibitive expensive soluble P [4]. PR is acid-soluble and activities that increase rhizosphere acidification increase its solubility. Nitrogen fixation is one such aspect that significantly lowers rhizosphere pH [5, 6]. In the light of the proceeding, a field experiment will therefore be conducted to investigate the effect of the acids secreted by cowpeas (*Vigna unguiculata*) into the rhizosphere (during the biologically nitrogen fixation process) on Minjingu PR solubility as well as the subsequent contribution to the plant available P fraction, and on P uptake by the crop. The use of rock phosphate for gardens is a common practice for both flowers as well as vegetables. Flowers and vegetable respond to application of rock phosphate early in the season and will reward you with big, vibrant blooms. Phosphorus deficiency has been identified as one of the major soil fertility constraints in the soils [7]. Many small-scale farmers in the zone find it increasingly difficult to afford water-soluble commercial P fertilizers because of high cost. Hence, the need to increase crop production with less expensive indigenous phosphate rocks (PRs) merits the attention of local researchers. Large deposits of phosphate rock exist in West Africa [8], and their application to increase crop production has been investigated with varying degree of success [9].

Phosphorus (P) is needed in virtually all metabolic processes such as energy transfer, signal transduction, macro-molecular biosynthesis, photosynthesis and respiration [10]. It is, however, one of the least available and least mobile mineral nutrients to plants in many cropping environments, based on its contribution to the biomass as a macronutrient [11]. Extremely low levels of available phosphorus in the rhizosphere make it one of the major growth-limiting factors in many ecosystems [12]. Phosphate fixation increases significantly in acid soils, which accounts for nearly 26% of the world's soils [13]. As a consequence of organic and inorganic fixation, nearly 80% of applied Pi may be unavailable to plants [14]. This problem is especially acute in tropical regions, particularly Africa, where production of crops without fertilizer application is resulting in continuous mining of essential nutrients by plants. Furthermore, at the current world- wide rate of fertilizer application, the readily available sources of high-grade phosphate rocks may be depleted within the next 60 to 90 years [15]. Increasing population and extension of agriculture to low- and marginal-fertility lands will further increase the demand for the precious supply of phosphate fertilizers. Potential symbiotic nitrogen fixation (SNF) in these heavily weathered acid soils of tropical and semi-humic tropics is limited, since P is generally deficient hence limits the nodulation [15]. Therefore, the objective of this study was to determine the rate of P dissolution from rock phosphate using elemental sulphur, oxalic acid and phosphoric acid as acidulating agents.

2.0 Materials and methods

The experiment was carried out at Kenyatta university farm, Kiambu County, Kenya. The site lies at an altitude of 1745 meters above sea level and is within latitude 110 0.012 S and longitude

3649 59.880 E. The average amount of rainfall received is 989 mm per year where 1200 mm rains is recorded during the long rains whereas 780 mm is recorded during the short rains [16]. Temperature ranges between 12.8 degrees Celsius during the cold month and 24.6 degrees Celsius during the hot seasons. The soils are loamy, acidic, well drained and moderately deep [17].

2.1 Experimental Design, layout and Data collection

A set of laboratory experiments were conducted to investigate phosphate-dissolution ability from rock phosphate (PR) in soil through application of organic acids (oxalic and phosphoric acid) and elemental sulphur. The soil was collected from Kenyatta university Agricultural farm. An incubation experiment was conducted in an aerobic environment at Kenyatta University, Agricultural Science and Technology laboratory in a completely Randomized Design, with six treatments with four replications. This was a single factor experiment. Treatments applied consisted of the control (bare soil); Rock Phosphte (RP) and soil; RP, soil and oxalic acid; RP, soil and phosphoric acid; phosphoric acid and soil; RP, soil and elemental sulphur. The treatments were thoroughly mixed with 200 g of soil, 400 mg of PR and 60 ml of the desired solvent. A 2 g elemental sulphur was used as described by Ghosal *et al*. [18]. Three sets of the experiment were incubated for three different periods; 30 days, 60 days and 90 days. This helped to compare the solubility of MPR in different solvents. The solvent with highest solubilising ability was used to grow the vegetables in the field. The mixtures were filled into polythene containers and then irrigation was carried out when necessary to maintain soil moisture content within the soil field capacity using deionised water. Weight of all the filled containers was registered for further reference during readjustment to the initial level of moisture content of the incubated soils. The filled containers were left open at a room temperature (25^0 C) [18]. The experiment lasted for three months. Only Soil samples were taken at different incubation time namely, 0, 30 60 and 90 from starting experiment, for determination of available P using the method described by (Bray 1). An aliquot of 5 ml was taken per treatment and its phosphate (available P) content determined following the standard procedure [16].

2.2 Data Analysis

Data collected was managed in excel spreadsheet and subjected to Analysis of Variance using SAS software. Significant differences between means were separated using Fischer's Protected Least Significance Difference (L.S.D) test at 5% level of significance. Linear regression on the rate of phosphorous dissolution was also determined.

3.0 Results and Discussion

3.1 Rate of phosphorus dissolution

The different dissolution agents showed significant differences on the rate of dissolution of phosphorus from the rock phosphate during an incubation period of 30 days. Elemental sulphur treatment had the highest dissolution of phosphorus from the rock phosphate recording 37.5 ppm. This was followed by phosphoric acid and Oxalic acid that had moderate effects on dissolution of phosphorus form rock phosphate each recording 12.42 ppm and 12.03 ppm respectively as illustrated in figure 1. The control had the least effect as it recorded a lower rate of phosphorous recording 5.37 ppm.

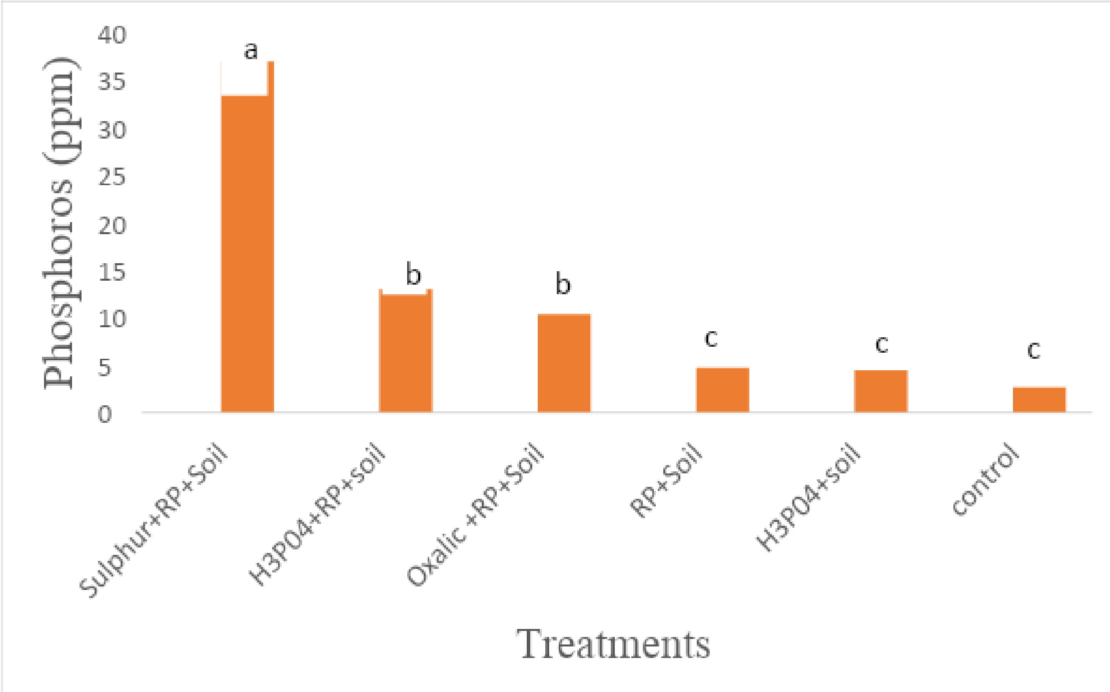

Figure 1: The phosphorus dissolution rate at 30 days after incubation on the various treatments

At sixty and ninety days, sulphur was superior in increasing the rate of phosphorus dissolution from rock phosphate with the highest value being obtained at 90 days with 1822.9 ppm as shown in table 1. This was more than 50% increase from that observed at day sixty (Table 1) while the other acidulating agents did not differ significantly with lower dissolution rates of phosphorus of lesser than 50 ppm with the control showing only 13.6 ppm.

Table 1: The influence of acidulating agents on the dissolution rates of phosphorus from rock phosphate

Treatments	30 days ppm	60 days ppm	90 days ppm
Sulphur+P+Soil	37.5[a]	1175.3[a]	1822.9[a]
H_3PO_4+RP+Soil	12.42[b]	16.6[b]	42.9[b]
Oxalic+RP+Soil	12.03[b]	14.9[b]	39.2[b]
RP+Soil	7.86[c]	14.0[b]	35.6[b]
H_3PO_4+Soil	6.05[cd]	11.6[b]	19.9[b]

Control	5.37^{d}	7.80^{b}	13.6^{b}
L.S.D	**1.95**	**162.0**	**220.0**

Means followed by the same letter within the same column are not significantly different (P≤0.05).

The trend of P-release by the fertilizers was more pronounced for the treatments with soil. The results on P release thus showed that maximum release of P from the unacidulated and partially acidulated rock phosphates needs some more periods of incubation for thorough acidulation of the fertilizer with the extractant to come into equilibrium with P in solution. Higher solubility of the PRs in sulphur possibly results from higher reactivity rather than from any difference in surface area presented for dissolution [19]. Such results were confirmed by Gholizade et al. [20] who found that P- adsorption occurs rapidly in the first period and followed by a slow adsorption processes, reaching the soil to equilibrium after 50 days. While found that the state of equilibrium in some sedimentary soils occurred during two days only.

3.2 Linear regression on influence of acidulating agents on phosphorus dissolution in soil

All the acidulating agents used in evaluating their effects on dissolution of phosphorus in soil has a positive correction as indicated by the high R^2 values. However, there were no significant differences observed when compare to the control. Sulphur + Soil had the higher rate of dissolution with a R^2 value of 0.997, this was followed by rock phosphate +soil with the R^2 value of 0.956 figure 2. Phosphoric acid had the least dissolution rate effect recording R^2 value of 0.882 during the 90 days incubation period. Phosphate rocks (PRs) are suitable for direct application as a possible alternative to more expensive soluble phosphate fertilizers in agricultural fields. But the ability of the PRs to release phosphates in the plant available forms depends on the particle size and chemical and mineralogical characteristics of the PRs as well as the properties of the soil in which they are applied. The principal mineral in most PR sources is apatite, but it varies widely in physical, chemical, and crystallographic properties.

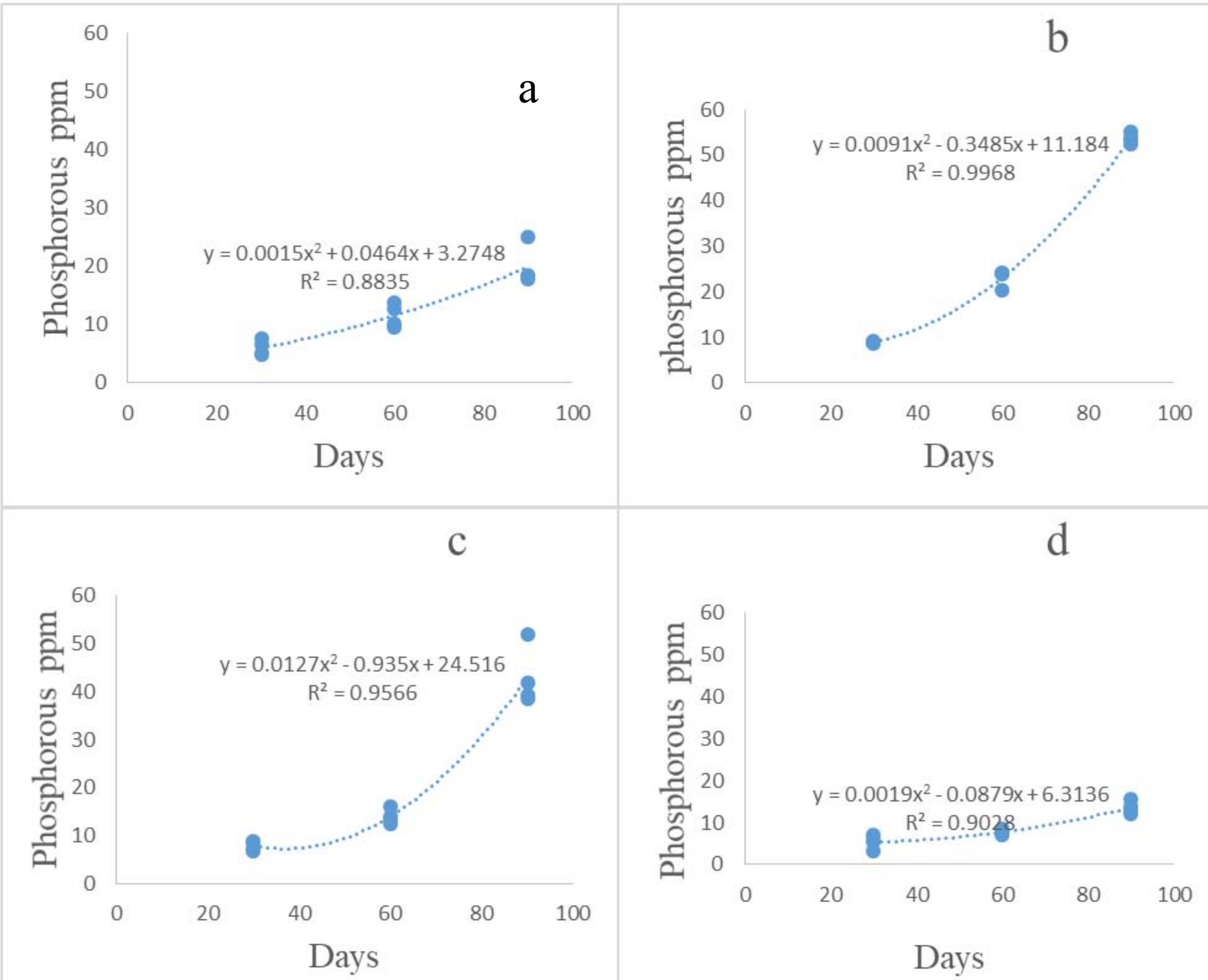

Figure 2: Regression analysis as a polynomial function of the acidulating agents on phosphorous dissolution from rock phosphate for a period of 90 days. (a)H_3P0_4+soil, (b) Oxalic+Soil, (c) Sulphur+Soil, (d) control

3.3 Relationship between phosphorus dissolution rate from rock phosphate by different acidulating agents in 90 days incubation period.

The acidulating agents exhibited a positive relationship as exhibited by the regression polynomial function in figure 3. All the treatment led to an increment in the rock phosphate with the 90 days incubation period. Sulphur + soil + rock phosphate had the highest effect on phosphorus with the R^2 value being 0.917 having obtained 2049.499 pmm of phosphorus concentration in the soil. The phosphoric acid was the second bests with extremely lower levels compared with Sulphur and rock phosphate (Figure 3). The control had the least dissolution rate of phosphorus but had a high R^2 value (R^2= 0.902) as shown in figure 3.

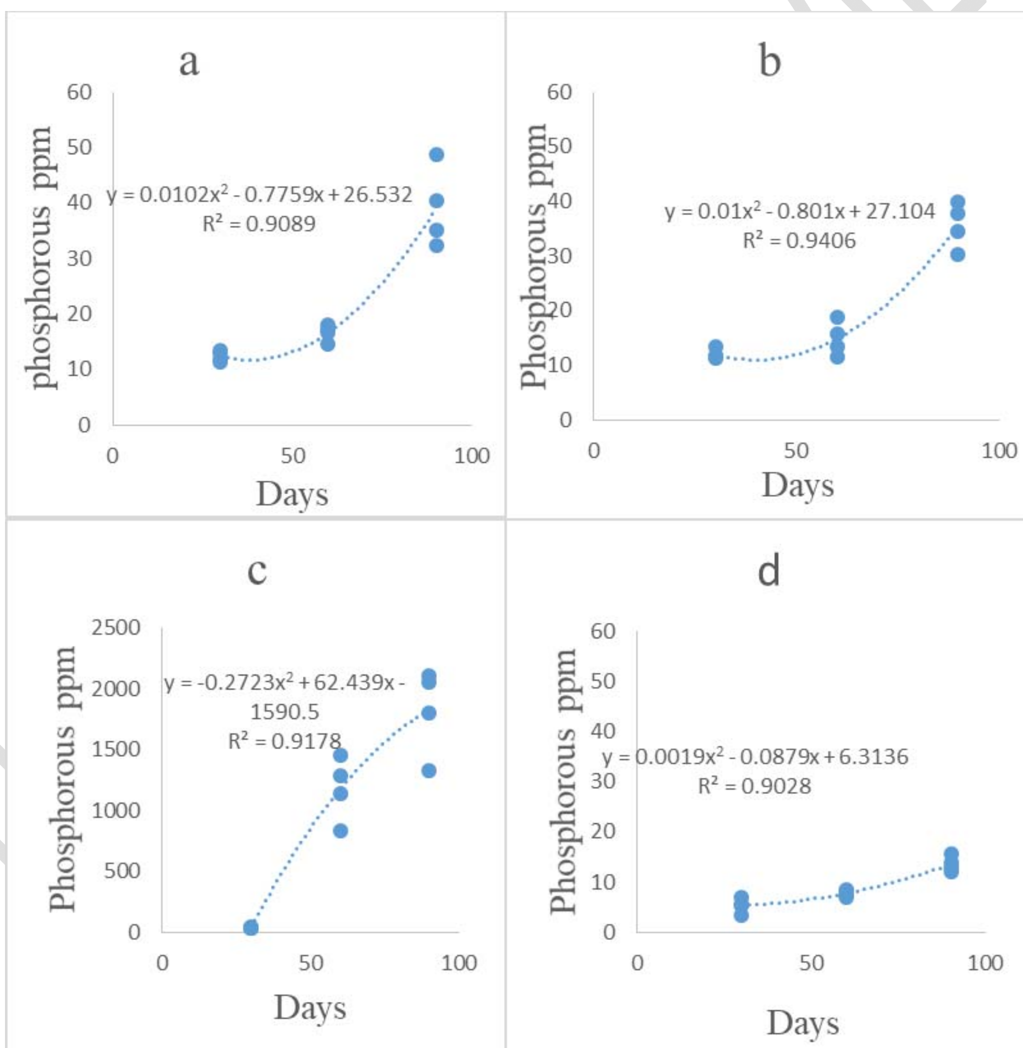

Figure 3: Regression analysis as a polynomial function of the acidulating agents on phosphorous dissolution from rock phosphate for a period of 90 days. (a)H_3P0_4+RP+soil, (b) Oxalic+RP+Soil, (c) Sulphur+RP+Soil, (d) control

The solubilization of rock phosphate is an indication of chemical and mineralogical characteristics specific for specific P minerals hence making it available to the crops. Reactivity or solubility is a measure of the rock phosphate ability to release phosphorus (P) for plant uptake. Gholizadeh *et al*. (19) reported that to avoid time, trouble and cost of doing field trials for determining the reactivity of PRs, solubility of these in different acidulating agents could be a criterion for predicting their reactivity. The 'wet process' for the production of phosphoric acid (H_3PO_4) commonly refers to the dissolution of phosphate rock by sulphuric acid (H_2SO_4) [21]. The acidulation solid by product formed as a resultant of this process is phosphogypsum ($CaSO_4.2H_2O$). The superphosphate acid concentrate treats further phosphate rocks to form triple superphosphate (TSP) fertilizers (40-48% P_2O_5). The addition of ammonia (NH_3) forms ammonium phosphate (46-48% P_2O_5) [22].

The standard for acidulation has been sulphuric acid because of cost and availability. Phosphogypsum is a by-product waste from this process. For every ton of phosphoric acid produced from sulphuric acid acidulation there are five tons of phosphogypsum produced. Kumari and Phogat [23] reported that plants influence the rate of rock phosphates dissolution by the secretion of acid or alkali, and production of chelating organic acids (citric, malic and 2-ketogluconic acid). Plant species differ in their P uptake, demand and their ability to absorb soil solution P [24]. Additionally, Plant species exhibit differences in their ability to access sparingly forms of P that are unavailable to other plants. According to Bagavathi *et al*. [24], the mechanism whereby high rooting density per se stimulates RP dissolution is probable related to the lowering of the concentration of Ca^{2+} and $H_2PO_4^-$ in the solution surrounding the surface of the RP particles. Studies indicated that reactive RPs may have potential applications in alkaline soils when crop such as rapeseed (*Brassica napus*) which is organic-acid secreting is cultivated on it.

The findings of this study also agrees with those of Mnkeni *et al*. [25] and Weil [26], rapeseed is able to increase the solubilization, even from less reactive RP sources. Partially acidulated rock phosphates (PARP) are rock phosphates which have been acidulated with sulphuric or phosphoric acid with less than the stoichiometric quantity of acid needed for making SSP or TSP. It was reported that that 40-50 % acidulation of less reactive rock phosphate with sulphuric acid or 20 % acidulation with phosphoric acid is appropriate for increasing efficiency of rock phosphate [27]. Miri, [28] reported that P recovery in the soil was 0.25 % for the North Carolina rock phosphate, whereas it ranged between 1.2-1.6 % for the corresponding 50 % PARP. The agronomic effectiveness of PARP has been found to be pronounced than rock phosphate. Further, Camenzuli, [29] used rock phosphates acidulation with $H_2PO_4^+$ HNO_3 in the ratios of 3:1, 1:1 and 1:3 on Vigna mungo. Dry matter yield and P uptake was found highest in PARP which was acidulated in the ratio 3:1. The findings of this study also agree with those of Bagavathi Ammal *et al*. [24]who reported an increase in the rate of dissolution and efficiency of low grade Udaipur rock phosphate when mixed with elemental sulphur (S) in a ratio of 5:1 and tested on onion–black gram sequence grown on soil having pH of 7.7. The results showed significant increase in available P, due to microbial oxidation of S leading to production of protons (H^+) which dissolved rock phosphate-P and increased available P content.

4.0 Conclusions and Recommendations

The acidulating agents showed significantly increase different dissolution rates of P from rock phosphate with sulphur showing the highest concentration after 90 days. The phosphoric acid and oxalic acid had P dissolution effect on rock phosphate but much lower to that exhibited by sulphur. Therefore, the study highly recommends that sulphur as an acidulating agent is a viable option and can significantly increase the solubility of phosphorus in rock phosphates to benefit agricultural systems.

References

1. Havlin, J. L., Tisdale, S. L., Nelson, W. L., and Beaton, J. D. (2016). *Soil fertility and fertilizers*. Pearson Education India.
2. Gouda, S., Kerry, R. G., Das, G., Paramithiotis, S., Shin, H. S., and Patra, J. K. (2018). Revitalization of plant growth promoting rhizobacteria for sustainable development in agriculture. *Microbiological research*, *206*, 131-140.
3. Jama B and Van Straaten P. (2006). Potential of East African Phosphate Rock Deposits in Integrated Nutrient Management Strategies. *Anais da Academia Brasileira de Ciencias* 78(4):781-790
4. Zapata F and Roy R.N (2004). *Use of phosphate rock for sustainable food and agriculture*: United Nation. 12-121.
5. Marschner H. *Mineral Nutrition of Higher plants*. Academic Press, London, UK, 1995; 889.
6. Filbert L. Ahmat; Jayne N. Mugwe; Stephen K. Kimani, and Joseph P. Gweyi-Onyango. Maize response to *Tithonia diversifolia* and rock phosphate application under two maize cropping systems in Kenya. Journal of Applied Biosciences 2014; 79:6983 – 6991. ISSN 1997–5902
7. Rao, I. M., Miles, J. W., Beebe, S. E., & Horst, W. J. (2016). Root adaptations to soils with low fertility and aluminium toxicity. *Annals of Botany*, *118*(4), 593-605.
8. Hellal, F., El-Sayed, S., Zewainy, R., & Amer, A. (2019). Importance of phosphate pock application for sustaining agricultural production in Egypt. *Bulletin of the National Research Centre*, *43*(1), 11.
9. Margenot, A. J., Singh, B. R., Rao, I. M., & Sommer, R. (2016). Phosphorus fertilization and management in soils of sub-Saharan Africa. *Soil Phosphorus, CRC Press, Boca Raton*, 151-208.

10. Liu, S., Meng, J., Jiang, L., Yang, X., Lan, Y., Cheng, X., & Chen, W. (2017). Rice husk biochar impacts soil phosphorous availability, phosphatase activities and bacterial community characteristics in three different soil types. *Applied Soil Ecology*, *116*, 12-22.
11. Sardans, J., Alonso, R., Janssens, I. A., Carnicer, J., Vereseglou, S., Rillig, M. C., ... & Penuelas, J. (2016). Foliar and soil concentrations and stoichiometry of nitrogen and phosphorous across European Pinus sylvestris forests: relationships with climate, N deposition and tree growth. *Functional Ecology*, *30*(5), 676-689.
12. Pel, R., Dupin, S., Schat, H., Ellers, J., Kiers, E. T., & van Straalen, N. M. (2018). Growth benefits provided by different arbuscular mycorrhizal fungi to Plantago lanceolata depend on the form of available phosphorus. *European journal of soil biology*, *88*, 89-96.
13. Herrera-Estrella, L., & López-Arredondo, D. (2016). Phosphorus: The underrated element for feeding the world. *Trends in plant science*, *21*(6), 461-463.
14. Yakti, W., Andrade-Linares, D. R., Ngwene, B., Bitterlich, M., Kovács, G. M., & Franken, P. (2019). Phosphate Nutrition in Root–Fungus Interactions. *Endophytes for a Growing World*, 120.
15. Kataki, S., West, H., Clarke, M., & Baruah, D. C. (2016). Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. *Resources, Conservation and Recycling*, *107*, 142-156.
16. Vance C. (2001). Symbiotic nitrogen fixation and phosphorus acquisition, plant nutrition in world of declining renewable resources. *Plant Physiol*, 127: 390-397
17. Ogembo (2015). Laboratory Methods of Soil and Plant Analyses: A Working Manual (2nd Ed.). Nairobi, Kenya. Partey of Africa in relation to productivity. Geoderma, 77:1-
18. Ghosal, P. K. and Chakraborty, T. (2012). Comparative Solubility Study of Four Phosphatic Fertilizers in Different Solvents and the Effect of Soil. *Resources and Environment* 2012, 2(4): 175-179.
19. Taylor, D. P., & Haun, G. W. (2018). *U.S. Patent Application No. 15/884,490*.
20. Gholizadeh A, Ardalan M, Tehrani M M, Hosseini H M, Karimian N, "Solubility test in some phosphate rocks and their potential for direct application in soil", *World Applied Sciences Journal* vol.6, no.2, pp.182-190, 2009.

21. Singh, D. K., Singh, S., Kumar, V., & Kumar, A. (2018). Impact of phosphorus and Sulphur organo mineral fertilizers on growth and yield attributes of green gram (Vigna radiate (L.) Wilczek) on alluvial soil. *IJCS*, *6*(2), 2983-2987.

22. Jazaeri, M., Akhgar, A., Sarcheshmehpour, M., & Mohammadi, A. H. (2016). Bioresource efficacy of phosphate rock, sulfur, and Thiobacillus inoculum in improving soil phosphorus availability. *Communications in Soil Science and Plant Analysis*, *47*(11), 1441-1450.

23. Kumari, K., & Phogat, V. K. (2008). Rock phosphate: Its availability and solubilization in the soil–A review. *Agricultural Reviews*, *29*(2), 108-116.

24. Bagavathi Ammal, U., Mathan, K. K. and Mahimairaja, S. (2001). Effect of different levels of rock phosphate-sulphur granule on yield and nutrient availability. *Indian J. Agric*. *Res.*, 35(3): 166-170.

25. Mnkeni, P. N. S., Chien, S. H., and Carmona, G. (2000). Effectiveness of Panda Hills phosphate rock compacted with triple superphosphate as source of phosphorus for rape, wheat, maize, and soybean. Communications in Soil Science & Plant Analysis, 31(19-20), 3163-3175.

26. Weil, R. R. (2000). Soil and plant influence on crop response to two African phosphate rocks. Agron. J., 92: 1167-1175.

27. Moneim, A. I., Moussa, S. A., & El-Edfawy, Y. M. (2015). Effect of rock phosphate along with elemental sulfur, organic manure and bio-fertilizer on quantitative and qualitative characters of canola (BRASSIA NAPUS L.). *International Journal of Academic Research*, *7*.

28. Miri, C. (2015). Studies on Phosphorus Release From Some Rock Phosphates Under Chemical and Biological Treatments (Doctoral dissertation, Indira Gandhi Krishi Vishwavidyalya, Raipur).

29. Camenzuli, D. (2015). Development of orthophosphate and silica treatments for the management of environmental contaminants at Wilkes landfill, East Antarctica.