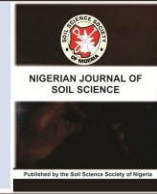




Nigerian Journal of Soil Science

journal homepage: www.soilsjournalnigeria.com



PHOSPHORUS AVAILABILITY FROM THERMALLY ALTERED PHOSPHATE ROCK

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ABSTRACT

Several studies have shown that the effectiveness of phosphate rock (PR) as phosphorus source for direct application is largely determined by the extent of its dissolution in moist soil. An incubation experiment was carried out in the Soil Science laboratory of Obafemi Awolowo University to monitor the rate of P release from thermally altered Ogun phosphate rocks (OPR) and mineral P fertilizers (SSP). Four sources of phosphorus (P) were used: OPR with Na₂CO₃ in ratio 2:1 at 900 °C (TOPR); OPR without Na₂CO₃ at 900 °C (UOPR); OPR alone at ordinary temperature (NOPR) and single superphosphate (SSP); three rates of each phosphate rock source (0, 30, and 60 Kg ha⁻¹) were used on soil samples with varying pH values. Soil pH and available P were determined in all the treated samples every fortnight for six weeks. There was no significant difference at $p \leq 0.05$ in the available P and the pH values among all the treatments. Soil samples treated with SSP had the highest value for available P at 2nd week of incubation while samples treated with TOPR had the highest P values at 4th and 6th week of incubation in all the treated samples. Hence, thermal treatment of the mixture of phosphate rock and Na₂CO₃ in 2:1 ratio at 900 °C enhances rate of P release irrespective of soil pH value.

INTRODUCTION

Phosphorus is commonly a limiting nutrient for plant growth in many soils around the world (McDowell and Stewart, 2006). In Nigeria, the deficiency of P is so extreme in many soils that without adequate application of this element, investment in other agricultural technologies may not be effective to increase crop production and to contribute to food security (Akinrinde *et al.*, 2003). Huge amount of money is spent on annual basis on importation of mineral P fertilizer to augment local production yet are still in limited supply, this represent a major outlay for resource-poor

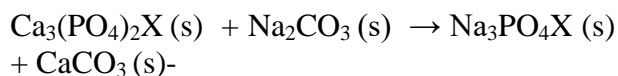
farmers. In addition, intensification of agricultural production, due to increasing population, expensive fertilizer inputs, short to non-existing fallow periods necessitate the addition of P inputs not only to increase crop production but also to improve soil P status in order to avoid further soil degradation. Therefore, it is imperative to explore alternative P inputs, The direct application of PRs is an agronomic and economically sound alternative to the more expensive superphosphates in the tropics if locally available (Chien, and Hammond 1978; Rajan

et al., 1994; Chien, and Menon, 1995b; McLay *et al.*, 2000; Sekhar and Aery, 2001; Odiete *et al.*, 2005; FAO, 2006; Taalab and Badr, 2007 and Adesanwo *et al.*, 2011).

Phosphate rock deposits exist in four sedimentary basins in Nigeria (Ogun, Osun, Edo, Sokoto). Several studies have shown that the effectiveness of phosphate rock (PR) as phosphorus source for direct application is largely determined by the extent of its dissolution in moist soil. Phosphate rocks (PRs) have been used as a source of phosphorus (P) for direct application on acid soils in Nigeria as alternatives to superphosphate and found viable compared to mineral P fertilizer.

Various methods have been used to improve the solubility of PR and thus, increase its widespread implementation. These include: (i) partial acidulation with H₂SO₄ or H₃PO₄ (Adediran and Sobulo, 1998), (ii) mechanical activation (Jose, 1999). (iii) Biological means such as composting organic wastes with phosphate rocks (phospho-composts), (iv) thermal treatment (Lehr, 1980; Rautaray *et al.*, 1995) but the latter method is thought to be safe and cheap if adopted. Lehr (1980), suggested the possibilities of thermal alteration of apatite by addition of many chemicals such as chlorides, carbonates, silicates and sulphates of alkali metals and alkali earth metals at different temperature. Previous work carried out to test phosphorus supplying power of three phosphate rock materials (Ogun, Sokoto and Togo) at varying combination with two soluble salts (Na₂CO₃ and KCl) heated for two hours at three temperature ranges (300, 600 and 900 °C) showed that mixture of OPR and Na₂CO₃ (2:1) at 900 °C gave the highest P value in water. (Adesanwo and Akinremi, 2010 unpublished). The heat treatment partially transform the rock mineral into citrate soluble form thus, increasing availability of P to crops (Lehr, 1980). However, this thermal treatment method is yet to be tested in Nigeria.

Reaction Mechanism



The law of mass action indicates that decreasing the activity of Ca²⁺ or the P-species respectively will enhance apatite dissolution. By decreasing the Ca²⁺ and or P concentrations, the reaction will be 'pulled' from left to right. Since the goal is to enhance the P concentration in soils, a useful way to pull the dissolution reaction from left to right is by decreasing calcium ion concentrations in the soil solution. The focus of this research work was to substitute Calcium in the apatite mineral with Sodium (Na) via a double decomposition reaction at high temperature. (Note: Most sodium salts are soluble under any condition).

The objective of this work was to determine the rate of release of phosphorus from thermally altered Ogun phosphate rocks

MATERIALS AND METHODS

The incubation experiment was carried out at Obafemi Awolowo University Soil Science laboratory. Soil samples (0 - 15 cm depth) with varying pH values and under different management practices were collected from three different locations at Obafemi Awolowo University Teaching and Research farm namely: acidity and fertility sites, soil samples were also collected from fallow site. Treatments consisted of four sources of P: (i) OPR with Na₂CO₃ in ratio 2:1 heated to 900 °C for 2 hours (TOPR); (ii) OPR without Na₂CO₃ heated to 900 °C for 2 hours (UOPR); (iii) OPR alone at ordinary temperature (NOPR) and (iv) single superphosphate (SSP). One hundred grammes (100 g) air dried soil samples were weighed into transparent plastic cups and mixed thoroughly with each P source at the rate of 0, 30, and 60 Kg ha⁻¹ except SSP that was at the rate of 0 and 30 Kg ha⁻¹. The treatments were arranged in Completely Randomized Design (CRD) in duplicates. The soils were moistened to field capacity with

water and left for six weeks. Duplicate samples were terminated every two weeks. Soil pH and available P in the soil samples were determined.

Laboratory analysis

Soil analysis

Physical and chemical properties such as particle size analysis, pH, organic matter, exchangeable cations and available P were determined in the soil samples prior to the incubation experiment. Soil pH was determined in 0.01M (ratio 2:1 soil: CaCl₂) using glass electrode pH meter. Exchangeable bases (K, Na, and Ca) were determined by extraction with 1 N NH₄OAc at pH 7 at soil to solution ratio 1:10. Potassium, calcium and sodium in the extract were read by flame photometer. Particle size distribution was determined by the hydrometer method using sodium hexametaphosphate as the dispersing agent (Bouyoucos, 1962). Organic carbon was determined by wet oxidation (Walkley and Black, 1934). Available P was determined using 0.03 N NH₄F in 0.025 N HCl as extractant (Bray and Kurtz, 1945).

RESULTS AND DISCUSSION

Pre-Incubation

As shown in table 1, the soil pH for soil samples from acidity and fertility sites were moderately acidic (5.65) while the soil pH for sample from fallow site was slightly acidic (6.59). The percentage organic matter was lowest in soil sample from fertility site (3.56%) and highest in soil sample from fallow site (6.78 %). The soil sample from fallow site had the highest field moisture capacity of 20.63 % while soil sample from acidity site had the lowest field moisture capacity (14.45 %). The exchangeable K⁺ in soil sample from fallow, fertility and acidity sites were 0.44 cmol kg⁻¹, 0.23 cmol kg⁻¹ and 0.22 cmol kg⁻¹ respectively; exchangeable Na⁺ in soil sample from fallow, fertility and acidity sites were 0.32 cmol kg⁻¹, 0.20 cmol kg⁻¹ and 0.12 cmol kg⁻¹ respectively; exchangeable Ca²⁺ in soil

sample from fallow, fertility and acidity sites were 3.87 cmol kg⁻¹, 1.12 cmol kg⁻¹ and 0.96 cmol kg⁻¹. The available P in soil samples from acidity site was 8.85 ppm from fertility site 10.75 while from fallow site was 13.8 ppm. Samples from the three sites were loamy sand.

Incubation

The mean values for the available P and pH for the treated soil samples from three sites are shown in tables 2 and table 3. The pH value reduced gradually as the incubation period progresses while the available P increased in all the treated samples throughout the period of incubation. Application of different rates of P had no significant effect on soil pH at $p \leq 0.05$ in all the treated soil samples. Similar result was obtained with soil available P except during the 2nd week of incubation where a significant increase in soil available P was recorded for soil samples treated with mineral P fertilizer (SSP), this was as a result of its high solubility compared with thermally altered phosphate rock. Gradual increase in available P was observed in all the soil samples from the 4th to 6th week of incubation for soil samples treated with TOPR where the highest value in soil available P was recorded. An increase of 14 % and 7.7 % in soil available P with TOPR treated sample over SSP, 10 % and 31 % over UOPR and 12 % and 39 % over NOPR during the 4th and 6th week of incubation respectively with soil samples from acidity sites, similar result was obtained with samples from fertility and fallow sites. The increase in available P of TOPR with time agreed with the earlier work carried out by Lehr (1980); Adesanwo and Akinremi (2010 - unpublished) that thermal treatment of PRs with Na₂CO₃ in the ratio 2:1 at 900 °C transforms the apatite mineral to citrate soluble material thus enhancing its solubility. Gradual decrease in pH values was recorded with all the treated soil samples throughout the incubation period this could be the reason for gradual increase in soil available P recorded

and confirms earlier work done. (Khasawneh and Doll, 1978).

Soil available P values from samples treated with phosphate rock combined with Na₂CO₃ in the ratio 2:1 at 900 °C (TOPR) were higher than sample treated with phosphate rock alone heated for two hours at 900 °C (UOPR), This revealed the significant effect of added salt in enhancing rate of release of P from the rock material. Conflicting values in soil pH were observed among samples from different sites, this could be attributed to differences in their soil properties.

Comparing the available P of each site, soil samples from fallow site gave the highest available P throughout the six weeks of incubation. This could be as a result of the high phosphorus status of the soil (Table 1)

and highest value was obtained with TOPR treated sample figures. 1, 2, and 3. Even though the pH was close to neutrality, yet highest value in available P was recorded, this was an outstanding achievement.

CONCLUSION

The result from this research showed the use of thermally treated PRs in combination with Na₂CO₃ (ratio 2 :1) at 900 °C for 2 hours proved as good alternatives to mineral P fertilizers because its solubility is not restricted by the soil pH. It is envisaged that the thermally altered phosphate rock will be cost effective and within the reach of farmers. However, more research should be carried out to test its agronomic effectiveness.

Table 1. Chemical and physical properties of the three soil management practices.

Properties/ Management Practice	Acidity	Fertility	Fallow
pH (0.01N CaCl ₂)	5.65	5.79	6.59
Organic Matter content (%)	3.78	3.56	6.78
Avail. P (ppm)	8.85	10.75	13.8
Exchangeable K ⁺ (cmol kg ⁻¹)	0.22	0.23	0.44
Exchangeable Ca ²⁺ (cmol kg ⁻¹)	0.96	1.12	3.87
Exchangeable Na ⁺ (cmol kg ⁻¹)	0.12	0.20	0.32
Field moisture capacity (%)	14.45	16.75	20.65
Soil texture	Loam sand	Loam sand	Loam sand

Table 2: The Means of available P for soil samples from all the three sites using different treatment for the six weeks

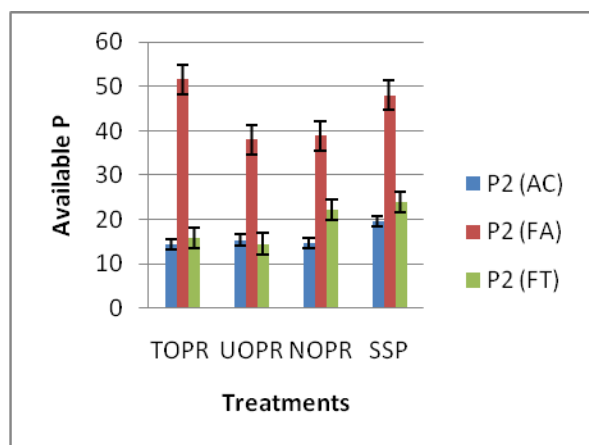
	Acidity site			Fertility site			Fallow site		
	Avail P (mg kg ⁻¹)			Avail P (mg kg ⁻¹)			Avail P (mg kg ⁻¹)		
	2 nd week	4 th week	6 th week	2 nd week	4 th week	6 th week	2 nd week	4 th week	6 th week
NOPR	14.78 ^b	19.10 ^a	40.23 ^a	14.55 ^b	14.55 ^b	59.88 ^a	38.93 ^a	40.37 ^a	70.33 ^a
UOPR	15.43 ^b	19.63 ^a	45.27 ^a	15.73 ^b	21.55 ^a	50.78 ^a	38.05 ^a	40.80 ^a	69.60 ^a
TOPR	14.35 ^b	21.93 ^a	65.85 ^a	22.18 ^a	22.73 ^a	68.13 ^a	37.17 ^a	51.58 ^a	75.08 ^a
SSP	19.55 ^a	18.90 ^a	60.75 ^a	24.00 ^a	26.00 ^a	56.70 ^a	36.70 ^a	47.93 ^a	64.95 ^a

*Within a row means with the same letter are not significantly different (LSD t test p=0.05).

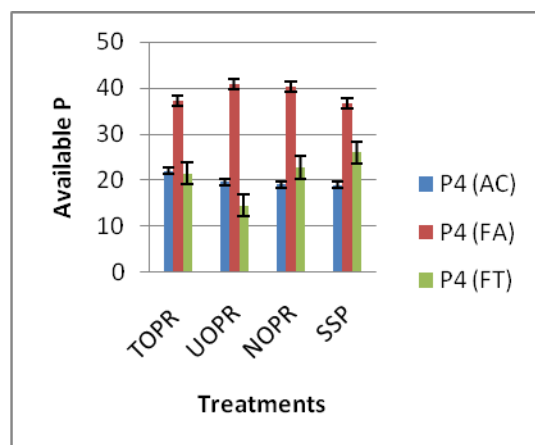
Table 3: The Means of pH values of the soil samples from all the three sites using different treatment for the six weeks.

	Acidity site			Fertility site			Fallow site		
	2 nd week	4 th week	6 th week	2 nd week	4 th week	6 th week	2 nd week	4 th week	6 th week
NOPR	5.47 ^a	5.93 ^a	5.93 ^a	5.73 ^a	5.57 ^a	5.37 ^a	7.16 ^a	7.12 ^a	7.11 ^a
UOPR	5.51 ^a	5.91 ^a	5.86 ^a	5.58 ^a	5.51 ^a	5.44 ^a	7.24 ^a	7.16 ^a	7.03 ^a
TOPR	5.47 ^a	6.01 ^a	5.97 ^a	5.60 ^a	5.48 ^a	5.45 ^a	7.26 ^a	7.19 ^a	7.11 ^a
SSP	5.45 ^a	5.45 ^a	5.45 ^a	7.21 ^a	7.11 ^a	6.98 ^a	7.21 ^a	7.11 ^a	6.98 ^a

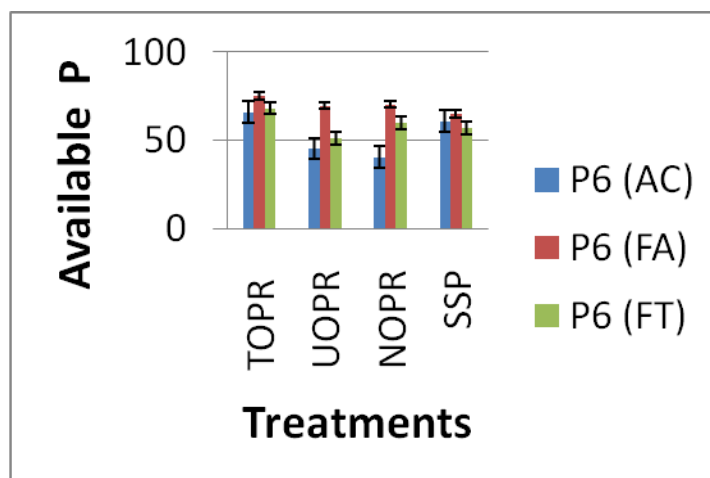
*Within a row means with the same letter are not significantly different (LSD t test p=0.05).



(1)



(2)



(3)

Figures 1, 2 and 3: Comparison of the available P in soil sample from the three sites (acidity: AC; fallow: FA and fertility: FT). 2 weeks (1), 4 weeks (2) and 6 weeks (3).

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