Application of Different Organic Acids on Phosphorus Solubility from Rock Phosphate

Aftab Jamal*, Azam Khan, Muhammad Sharif and Hifsa Jamal

¹Department of Soil & Environmental Sciences, Khyber Pakhtunkhwa Agricultural University, Peshawar, Pakistan

²Department of Chemistry, Abdul Wali Khan University, Mardan, Pakistan

aftabses98@gmail.com

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Abstract. An incubation experiment was conducted on P solubilization from rock phosphate (RP) through different organic acids such as oxalic acid, citric acid, acetic acid, humic acid and sulphur in the laboratory of the Department of Soil and Environmental Sciences, KP Agricultural University Peshawar during fall 2011. The experiment was laid in a complete randomize design. There were three replications with six treatments. The organic acids were used at the rate of 2 % for 50 g RP in 250 ml conical flasks. These samples were kept in an incubator at 25⁰c for four months and analysed for Mehlic-3 extractable P and pH values after 20 days interval. Statistical analyses were made and maximum P concentration of 1.52% was observed in the treatment of oxalic acid mixed with RP followed by the treatments of RP mixed with humic acid with P concentration of 0.368%. Rapid increases in P solubility from RP by mixing with oxalic acids were noted up to 60th days of incubation period and then remained stable after this period. Solubilization of P from RP by mixing with other organic acids was inconsistent. The pH in treatment of citric acid mixed with RP was noted as 5.64, followed by the treatments of oxalic acid with pH values of 6.31. A dramatic increase in pH value of 9.33 was observed in the treatment of RP mixed with humic acid. It is because the humic acid contains sodium salt and sodium hummate causes increase in its pH values.

Introduction

Phosphorus plays a dominant role in plant nutrition and development. Even though P is widely distributed in nature, yet in most of the soils P availability to the in soluble form is very limited, only 0.1% is available to plants [1]. In the form of phosphate fertilizers, phosphorous are added to the soil part of which is utilized by plants and almost more than 70% are converted into complexes such as iron phosphate, calcium phosphate and aluminium phosphate [2, 3]. Due to the high cost of phosphatic fertilizers there is a need for alternative sources. The practical use of rock phosphate (RP), in recent years attributes much attention of researcher in this regards to obtain more valuable products. At pH higher than 6 rock phosphate availability is restricted to the plants and bears lower yield as compared with the soluble phosphate [4, 5]. That is why the farmers hesitate to utilize RP directly.

Many traditional techniques are used such as thermal alteration or partial acidulation require substantial capital investments in order to increase the solubility of P from RP, however alternative approaches are also required to increase the availability of P from RP [5]. One approach for RP solubilization is the application of microorganisms able to excrete organic acids like oxalic acids, citric acids, acetic acids etc. It has been repeatedly shown that low molecular weight organic acids can strongly increase phosphorous solution concentration by mechanisms by creating favourable environment for P solubilization involving chelation and exchange reaction [7, 8]. Filamentous fungi are widely used as producers of organic acids [9, 10] and particularly mycorrhiza, [11], some *Aspergillus* and *pencillium* species have been tested by inoculating directly into the soil in order to solubilize RP [12, 13]. Inoculation of phosphate solubilizing mycorrhizal fungi improves the physico-chemical, biochemical and biological properties of RP amended soil [14].

In arid and semi-arid regions, the application of RP is not common because of alkaline nature, high pH, low organic matter as well as less solubility of P in these soils. Numerous investigations on soil pH, particle size of RP, and concentrations of Ca and P in soil solution have examined the solution of RP in soils and its subsequent effect on soil availability [15]. However, the availability of plant nutrients is limited in calcareous soils because of high base content coupled with high pH as well as the presence of carbonate minerals [16]. In calcareous soils P fertilizers shows less efficiency because of the reaction with Ca forming minerals such as di calcium phosphate dehydrate octa calcium phosphate and eventually hydroxyl-apatite [17]. Hence, sulphuric acid or phosphoric acid with RP is used to process chemically with the aim to convert into soluble phosphate fertilizers. Most soil microorganisms such as bacteria, fungi and actinomycetales have the capability to change insoluble phosphates to soluble forms.

Keeping in view the significance of organic acids to create favourable environment for P solubilization from RP, this incubation study was initiated to determine the degree extent of P solubilization from RP through mixing with different organic acids.

Materials and Methods

An incubation experiment was conducted on P solubilization from rock phosphate (RP) through different organic acids such as oxalic acid, citric acid, acetic acid, humic acid and sulphur in the laboratory of the Department of Soil and Environmental Sciences, KP Agricultural University Peshawar during 2011. The experiment was laid in a complete randomize design. There were three replications with six treatments. The organic acids were used at the rate 2 % for 50 g RP in 250 ml conical flasks. These samples were kept in an incubator at 25⁰c for four months and analysed for Mehlic-3 extractable P and pH values after 20 days interval.

The treatment combinations were as follows:

1. Rock phosphate (RP)
2. RP+ Oxalic acid
3. RP+ Citric acid
4. RP+ Acetic acid
5. RP+ Humic acid
6. RP+ Sulfur

Collection of Rock phosphate samples

Ground RP from Hazara region was brought into the laboratory of the Department of Soil and Environmental Sciences for this experiment.

Mehlic-3 Extractable P

Six g materials were taken into a 250 ml conical flask. Fifty ml Mehlic-3 extraction reagent was prepared by dissolving 138.9 g ammonium fluoride and 73.5 g EDTA in 1L pure water. The pH was adjusted as 2.0 ± 0.1 . The material was vigorously shaken for 5 min, filtered through whatman 42 filter paper. The P concentration of the filtrate was then assayed by using spectrophotometer.

pH values

Ten g materials and 50 ml distilled water was taken in a conical flask and materials water suspension (1:5) was made. The suspension was shaken for 30 minutes on mechanical shaker. The pH meter and room temperature were adjusted well. pH was noted by 105-ion analyser pH meter [18].

Results and Discussion

An incubation experiment was conducted to determine P solubilization from RP through different organic acids such as oxalic acid, citric acid, acetic acid, humic acid and sulphur in the

laboratory of the Department of Soil and Environmental Sciences, KP Agricultural University Peshawar during 2011. There were three replications with six treatments. The organic acids were used at the rate 2 % for 50 g RP in 250 ml conical flasks. These samples were kept in an incubator at 25°C for 120 days and were analysed for Mehlich-3 extractable P and pH after every 20 days interval. The data recorded during this investigation are presented in Table 1.

Table 1. Effect of organic acids on P solubility from RP with time.

Treatment	Dates of data recording					
	01/07/11	21/07/11	11/08/11	31/08/11	20/9/2011	10/10/11
Rock phosphate (RP)	0.124	0.412	0.108	0.039	0.052	0.025
RP+ Oxalic acid	0.642	0.96	1.40	1.48	1.50	1.52
RP+ Citric acid	0.195	0.159	0.18	0.13	0.50	0.136
RP+ Acetic acid	0.134	0.59	0.137	0.046	0.127	0.053
RP+ Humic acid	0.105	0.114	0.118	0.035	0.087	0.368
RP+ Sulfur	0.56	0.12	0.28	0.04	0.24	0.226

Table 1 illustrates the results of an experiment on P solubilization from RP through mixing with different organic acids such as oxalic, citric, acetic humic acid and sulphur. Statistical analyses were made for data regarding P solubility from RP indicate that maximum P concentration of 1.52% was observed in the treatment of oxalic acid mixed with RP followed by the treatments of RP mixed with humic acid with P concentration of 0.368% (Fig. 1). Comparatively more P was solubilized from RP through mixing with oxalic acids. Rapid increases in P solubility from RP by mixing with oxalic acids were noted up to 60th days of incubation period and then remained stable after this period. Solubilization of P from RP by mixing with other organic acids was inconsistent (Fig. 1).

Data regarding pH values are presented in Table 2 and Fig. 2. Data show a pH of 7.4 in the treatment having only RP after 120 days of incubation period but in other treatments where RP is mixed with organic acids such as oxalic, citric, acetic, humic acid and sulfur, pH values showed a steady decrease with a narrow range of fluctuation.

Table 2. Effect of organic acids on pH values.

Treatment	Dates of data recording					
	01/07/11	21/07/11	11/08/11	31/08/11	20/9/2011	10/10/11
Rock phosphate (RP)	8.29	8.11	8.44	7.89	7.74	7.4
RP+ Oxalic acid	5.82	6.01	6.11	6.25	6.22	6.31
RP+ Citric acid	6.01	6.28	5.84	6.22	5.7	5.64
RP+ Acetic acid	6.58	6.94	6.95	7.07	6.89	6.77
RP+ Humic acid	10.31	9.9	9.76	9.55	9.41	9.33
RP+ Sulfur	7.82	8.24	8.30	7.91	7.66	7.23

The pH in treatment of citric acid mixed with RP was noted as 5.64, followed by the treatments of oxalic acid with pH values of 6.31. A dramatic increase in pH value of 9.33 was observed in the treatment of RP mixed with humic acid. It is because the humic acid contains sodium salt and sodium hummate causes increase in its pH values. These results are in consistency with [19] who observed the similar results.

Figure 1. Effect of organic acids on P solubility from RP with time.

Figure 2. Effect of organic acids mixed with RP on pH values.

As most of the traditional techniques to increase the solubility of P from RP such as thermal alteration or partial acidulation require substantial capital investments, there is a need for alternative approaches to increase the availability of P from RP [6]. One approach for RP solubilization is the application of microorganisms able to excrete organic acids like oxalic acids, citric acids, acetic acids etc. It has been repeatedly shown that low molecular weight organic acids can strongly increase phosphorous solution concentration by mechanisms by creating favourable environment for P solubilization involving chelation and exchange reaction [7, 8]. Filamentous fungi are widely used as producers of organic acids [9, 10], and particularly mycorrhiza, [11], some *Aspergillus* and

penicillium species have been tested by inoculating directly into the soil in order to solubilize RP [12, 13]. Inoculation of phosphate solubilizing mycorrhizal fungi improves the physico-chemical, biochemical and biological properties of RP amended soil [14]. It has also been reported that the available P and aggregate stability levels, higher soil C levels, enzyme activities and lower soil PH were reported due to inoculation of these fungi.

Conclusions

Comparatively more P was solubilized from RP through mixing with oxalic acids. Rapid increases in P solubility from RP by mixing with oxalic acids were note up to 60th days of incubation period and then remained stable after this period. Solubilization of P from RP by mixing with other organic acids was inconsistent. Further research is suggested to solubilize P from RP mix with different organic acids to determine the extent and degree of their P solubility enhancement and their effects on growth of various crops in different agro-ecological zones of Pakistan.

Conflict of Interest

The authors declare that there is no conflict of interest.

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