Review Article

Biosolubilization of Phosphate Rock Using Organic Amendments: An Innovative Approach for Sustainable Maize Production in Aridisols - A Review

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Abstract | Phosphate rock is naturally occurring cheaper mean of phosphorus (P) availability but having drawback of poor solubility. Pakistan is a resource poor country. Economy of Pakistan mainly relies upon agriculture. Phosphorus (P) application (like other essential nutrients) is compulsory for getting higher yield. But availability of P is compromised in those soils having high pH and high calcium content. As at higher pH, conversion of P to plant unavailable forms take place. Chemical P fertilizers are needed to be applied at higher rate to fulfill crop demand. Farmers are unable to apply adequate levels of fertilizers due to poor economy and unavailability of fertilizers at the time of crop requirement. Among alternative cheaper sources of P, one is use of phosphate rock (PR). Pakistan is blessed with huge reserves of PR but poor solubility at higher pH makes it unsuitable for application as such. Thus, solubility of PR needs to be enhanced in a sustainable way. This review documented possible modes of PR dissolution for release of P. Possible means of PR dissolution and resultant P release include use of different organic amendments (*e.g.* farm yard manure, press mud, poultry dropping etc.), phosphorus solublizing bacteria and fungi as well as employment of plant growth promoting rhizobacteria *etc*.

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Introduction

Phosphate rock (PR) is the basic fundamental input required for manufacturing of all commercially available P containing fertilizers. At present, PR presents a trade name for more than 300 different P containing products available throughout the world. Carbonate, flouro, hydroxyl and sulpho apatites are the basic types of PR commonly found in rocks. There are two options for usage of PR. One is physically processed PR involving as such application of PR in raw form after grinding and sorting based on mesh size. Second option is chemically processed forms of PR by converting it into chemical P containing fertilizers. Problem associated with direct (as such) application of PR under high pH soils is occurrence of PR with alloy minerals (*e.g.* quartz, silica, iron and aluminum oxides *etc.*). Presence of these alloy minerals create hurdle in solubilization of PR thereby, lowering its solubility and P release.

Phosphorus; its importance and problem

Essentiality of P for plant growth is well known and well documented. For getting sustainable yield, exogenous application of P sources is compulsory. There are several functions of P in plants including involvement in cell metabolism, part of adenosine tri-phosphate (ATP), phospholipids, nucleic acid, DNA, RNA, role in synthesis of protein etc. Overall crop growth and yield particularly, root growth and development, formation of seeds and quality of crops is seriously affected due to deficiencies of P (Ezawa *et al*., 2002; Achal *et al*., 2007; Yadav and Pandey, 2018; Calle-Castañeda *et al*., 2018). Thus, provision of P is mandatory throughout the growing period of crops for getting sustainable yields (Grant *et al*., 2001). Many processes related to plant physiology such as photosynthesis, N-fixation, flower, fruit and seed formulation and crop maturity required an optimum supply of P. Plants deficient in P manifest symptoms like growth retardation, dark green, blue or purpling of leaves *etc*. (Brady and Weil, 2005).

Availability of P in soils

P exists in soils in two forms *i.e.* organic and inorganic. Generally, about 50 percent of total P is organic, however, variation exist in different soils (Brady and Weil, 2005). There is plenty of P present in agricultural soils ranging from 200-5000 mg kg^{-1} with an average of about 600 mg kg^{-1} (Gyaneshawar *et al*., 2002). However, less than 0.1% of this total P is plant available because of retention of this P with soil components such as Fe and Al oxides in low pH soils and Ca in high pH soils (Harris *et al*., 2006; Khan *et al*., 2010). Main factor responsible for availability of P to plants in soils is pH with maximum availability being noted at pH value of 6.5 to 7.5. At present, problem of low bioavailability of P to plants is among serious obstacle toward achieving agricultural sustainability as estimated yield losses due to shortage of P are 30-40% (Vance *et al*., 2003). Because of high pH and high Ca content of soils, insufficiency of P is also prevalent in Pakistan where more than 90% soils are declared as P deficient (having less than 100 mg kg^{-1} Olsen P), thus proper P management is essential for obtaining high yields (Ahmad *et al*., 2003; Aziz *et al*., 2006). Plants usually require higher supplies of P compared to native soil P content, therefore, exogenous application of P is done to fulfill this need. Total P present in soils are estimated to about 100-2000 mg kg^{-1}. Of which, 350-7000 kg ha^{-1} occur in plough layer, presenting small fraction of total P present in soils (Morel, 2002).

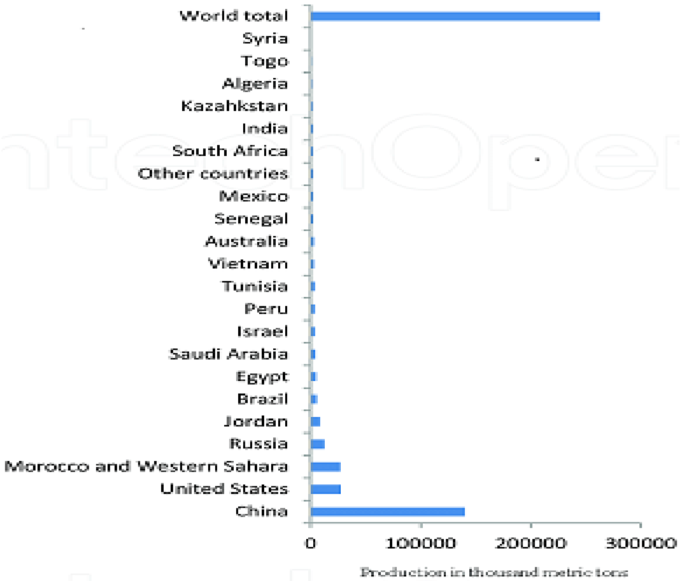

Figure 1: *Phosphate rock production worldwide in 2017, by country (in 1000 metric tons).*

Phosphate rock (PR)

Phosphate rock serves as main raw material for formulation of all commercially available P containing fertilizers. PR accounts for about 17.5 million tons of P source, 85% of which served as basic material for P fertilizers production (Cordell *et al*., 2009). Country wise PR production of the world is given in Figure 1 (Samreen and Kausar, 2019). Sedimentary rocks served as major source of phosphate rock being accounting for more than 80% PR (Uddin *et al*., 2012). From agronomic point of view, main concern is the phosphatic content of PR. Thus, more the P content of PR, more will be the credibility of PR. Conversion of PR to chemical fertilizer is impacted negatively by presence of impurities like carbonates, iron, magnesium, aluminum and chloride etc. However, such impurities do not matter in case if directly applied RP (Hammond and Day, 1992). High reactivity of flour apatite PR renders it most suitable to be used as P source (Khasawneh and Doll, 1978). Considerable deposits of PR existed in Khyber Pakhtunkhwa (KPK) province of Pakistan estimated to be 6.9 million ton as resource and 5.58 million tons PR serving as reserves (Sharif *et al*., 2013; Naseer and Muhammad, 2014; Abbasi and Manzoor, 2018).

PR could be employed in agriculture by two methods *i.e.* directly applied PR and PR used as a basic source of P fertilizers. Although direct application is cheaper, environmentally benign and preferred in organic farming but less reactivity and presence of impurities like Fe and Al content in low pH soils and Ca content in high pH soils renders it unsuitable for direct application (UNIDO and IFDC, 1998). In addition, not all types of PR are appropriate for all kind of soils and farming (Zapata, 2003). Low solubility of PR discouraged its use for direct application thus, compelling the scientists to explore other means of exploiting PR use in agriculture by enhancing its solubility and P recovery. Literature reported several methods of PR dissolution including use of organic amendments (FYM, pressmud, poultry manure, compost *etc*.), acid treatment of PR (partially), use of phosphorus solubilizing microorganisms (PSMs) etc. (Kumari and Phogat, 2008).

Factors affecting PR dissolution

Properties of PR: PR dissolution is greatly influenced by physio chemical properties of PR including mode of origin, particle size, thermodynamic stability, solubility and reactivity of PR (Vanlauwe *et al*., 2002).

Soil Factor: Solubilization of PR depends upon many soil and plants factors. Similarly, properties of PR also affect its dissolution ability. Various soil related parameters include proton provision ability of soil, pH of soil, CEC, soil Ca content, soil P concentration and organic fraction of soil. PR dissolution is more in soils with lower pH, less Ca on exchange sites and lower soil solution P (Vanlauwe *et al*., 2002). Soil with low pH (>5.5) values have greater ability of PR dissolution and P release (Bolan and Heldey, 1990). Higher organic matter proportion of soil also supports PR dissolution. This improvement can be attributed to higher CEC and release of organic acids from organic matter (Chien *et al*., 1990). Nying and Robinson (2006) also reported that PR dissolution is strongly affected by size of Ca sink in soil thereby by enhancing CEC and organic matter more effective dissolution could be accomplished. This can be attained by addition of organic amendments in soils.

Crop Factor: Differences exist among crops regarding P use from PR. Regarding crop factors influencing PR dissolution include P and Ca requirement of crop as well as ability of crop to acidify root surrounding area by secreting root exudates. Different crops have varying ability to uptake P from PR dissolution. Crops like maize, buckwheat, rape seed, leguminous and cruciferous family have more affinity for taking up P by RP dissolution (Baligar *et al*., 2001; Hocking, 2001). Secretion of many organic acids by their roots seems to be responsible for PR solubilization, P release and subsequent uptake by plant roots. Thus, PR can be applied under high soil conditions by employing such crops having ability to release organic acids and thereby have greater affinity for PR dissolution and P release by taking up Ca such as maize (Flach *et al*., 1987).

Mechanism of solubilization of phosphate rock

Soil phosphate occurs as apatite form (calcium phosphate) being fixed with soil constituents like Ca in alkaline soils. PR has low solubility and thus, having low P release and solubilization under alkaline soil pH (Goldstein, 2000). Such apatite or fixed P can be released by lowering of pH governed by various kinds of organic acids secreted by soil microbes (PSMs). Thus, organic acid secretions by plant roots and many strains of soil microorganisms (Fankem *et al*., 2006) seems to be the basic mechanism responsible for PR solubilization and subsequent P release from Ca-phosphates (Vassilev *et al*., 2006). Organic acids like acetic, citric and oxalic acids result in rhizosphere acidification and thus dissociation of apatite form of P like Ca-phosphate take place (Hinsinger, 2001; Kumari *et al*., 2008). Additionally, some inorganic acids like H_2SO_4, HCl and HNO_3 are also responsible for PR dissolution, thereby, commonly used for partial acidulation process of PR (Fekri *et al*., 2011). Mechanism of PR solubilization by acidulation can be depicted from following chemical reaction:

$12HNO_3 + Ca_{10}(PO_4)_6F_2 \text{--->} 3Ca(H_2PO_4)_2$[Monocalcium phosphate] + $10Ca(NO_3)_2 + 2HF$

Use of organic amendments as a tool for solubilization of rock phosphate; an innovative approach

Use of FYM for PR solubilization: It has been reported that use of FYM in combination with PR via co-composting technique resulted in PR dissolution and subsequently release of P. The product thus obtained is known as phosphate rich organic manure (PROM) which can be utilized as a replacement of commercial P fertilizer. In addition to increased P solubility, this product also prevents re-fixation of P (Sekhar *et al*., 2001). It was reported that combined use of FYM (0.5-4.0 MT ha^{-1}) and PR (40 kg ha^{-1}) could result in substantial improvement in P solubility from RP dissolution depending on soil reaction (Sekhar and Aery, 2001). In an experiment, Hellal *et al*. (2013) also reported an enhanced PR dissolution and P release resulted from integrated use of phospho-compost prepared from PR and FYM in maize crop. Similarly, Sharif *et al*. (2011) also documented the beneficial effects of co-composting of FYM and PR on enhanced PR dissolution and P solubility.

Use of poultry manure (PM) for PR solubilization: Poultry dropping are well reported organic manure enriched with essential nutrients. Impact of PM in terms of improving PR dissolution and P release has also been reported extensively. Boateng *et al*. (2006) claimed that integration of PR with PM can improve nutrient availability to greater extent. Similar results were reported by Farhad *et al*. (2009). Khan and Sharif (2012) also suggested that composting of PR with PM amended with effective microorganisms (EM) resulted in greater PR dissolution and P release. Similarly, Akande *et al*. (2005) documented an improvement in yield and P content of maize by combined application of PR with poultry manures. However, Mahimairaja *et al*. (1995) discouraged the utilization of PM for making compost with PR due to high Ca content of poultry manures that served as impurity and lowered the reactivity of PR.

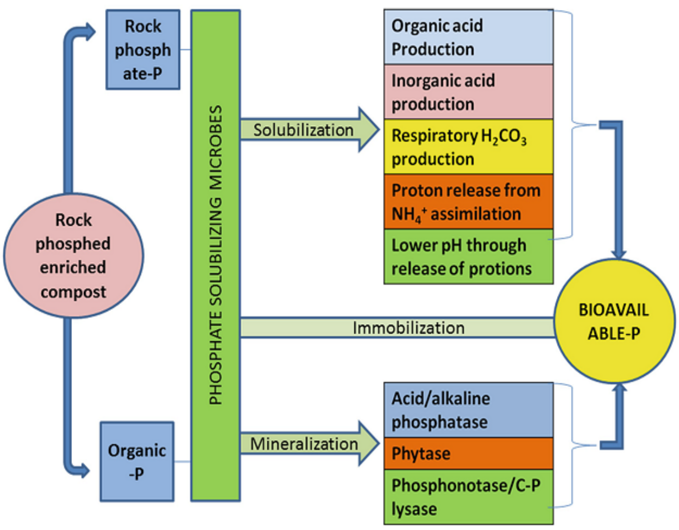

Figure 2: *Possible mechanism of PR solubilization through composting.*

Use of Compost for PR solubilization: Literature suggested that PR co-composted with organic stuff substantially improved the RP dissolution and P release. Composting can be performed by using any organic materials like FYM, green manure, poultry droppings, city waste etc. (Ali *et al*., 2014). Hellal *et al*. (2013) documented that application of PROM made from composting of PR with organic materials resulted in improved nutrient composition of soil and subsequent uptake by plants. Similarly, enhanced P release from PR dissolution was also noticed by the use of PROM. Outcomes of Zafar *et al*. (2012), Ahmad *et al*. (2006) and Rizwan *et al*. (2006) also supported positive impact of composted PR regarding availability of P for plant use.

Use of pressmud for PR solubilization: Among organic amendments pressmud is found to be more effective mean of PR solubilization. Pressmud is considered as a bio active source for solubilization of PR and P release particularly in high pH soils (Mahimairaja *et al*., 1995; Aziz *et al*., 2010). Many researched reported the beneficial role of pressmud in dissolution of PR for P release (Aziz *et al*., 2006; Aziz *et al*., 2010; Qureshi *et al*., 2014; Sabah *et al*., 2016; Sabah *et al*., 2018a; 2018b). It was documented that it is the higher quantity of sulphur present in pressmud that trigger PR dissolution by lowering soil pH (Joggi *et al*., 2005).

Use of PSMs for PR solubilization: Use of microorganisms for PR dissolution was documented first time in 1903 (Khan *et al*., 2007). Afterward, wide range research was carried out in this regard and many types of PSMs were explored for their ability to solubilize P from PR (Aseri *et al*., 2009). There is a bulk of PSMs present in soil depending on soil types. Bacteria account for half of microbial population while fungi contribute to 0.1 to 0.5% of microbial population in soil (Chen *et al*., 2006). Similarly, plant growth promoting rhizobacteria (PGPRs) are also reported having such ability P solubilization from RP dissolution. Keeping in view this ability of PSMs and PGPRs, extensive research work was performed to explore the beneficial strains (Gyaneshwar *et al*., 2002). Possible mechanism responsible for PR dissolution is the secretion of many types of organic and inorganic (HCl) acids as well as chelating compounds in the rhizosphere that resulted in lowering of soil pH as described in Figure 2 (Kim *et al*., 1997; Deubel *et al*., 2000; Moharana *et al*., 2018). Similarly, PSMs also secret many enzymes (phosphatises and phytases) that also assist PR solubilization (Goenadi *et al*., 2000; Tarafdar *et al*., 2003). Various strains of PSMs reported for PR solubilization include *Pseudomonas, Bacillus, Rhozobium, Enterobacter, Agrobacterium, Aspergillus, penicillium, Pseudomonas florescence etc*. (Kpomblekou and Tabatabai, 1994; Rodriguez and Fraga, 1999; Vessey *et al*., 2004; Hilda and Fraga, 1999; Panda *et al*., 2013). Among PGPRs strains like *Psedomonas*, *Azospirillum*, *Bacillus*, *Rhizobia*, etc. are well reported (Kloepper, 1994; Hall *et al*., 1999; Chabot *et al*., 1993).

Conclusions and Recommendations

PR is a naturally occurring cheaper source of P. Direct application of PR is not effective in alkaline soils due to less reactivity. PR solubilization can be improved by the employment of organic amendments like FYM, poultry manure, compost and pressmud. It was found that pressmud proved more effective organic amendment in terms of PR dissolution. Similarly, use of PSMs and PGPRs can also improve the P release from RP by enhancing its dissolution. Such an improvement in P release from PR could encourage usage of PR as a substitute the costly commercial P sources in poor countries like Pakistan.

Novelty Statement

The study recommnds that organic amendments improve P release from PR through biosolubilization.

Author's Contribution

Noor-us-Sabah: Designed and prepared the manuscript.
Mukkram Ali Tahir: Supervised the writeup.
Ghulam Sarwar: Technically assisted at every step.
Amir Aziz and Muhammad Zeeshan Manzoor: Helped in data collection.
Muhammad Luqman and Muhammad Aftab: Proof reading.

Conflict of interest
The authors have declared no conflict of interest.

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