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Review

Rock Phosphate Solubilizing Potential of Soil Microorganisms: Advances in Sustainable Crop Production

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Citation: Khoshru, B.; Nosratabad, A.F.; Mitra, D.; Chaithra, M.; Danesh, Y.R.; Boyno, G.; Chattaraj, S.; Priyadarshini, A.; Anđelković, S.; Pellegrini, M.; et al. Rock Phosphate Solubilizing Potential of Soil Microorganisms: Advances in Sustainable Crop Production. *Bacteria* **2023**, *2*, 98–115. https://doi.org/10.3390/bacteria2020008

Academic Editor: Bart C. Weimer

Received: 11 April 2023
Revised: 28 April 2023
Accepted: 8 May 2023
Published: 10 May 2023

Abstract: Phosphorus (P) is one of the most important elements required for crop production. The ideal soil pH for its absorption by plants is about 6.5, but in alkaline and acidic soils, most of the consumed P forms an insoluble complex with calcium, iron, and aluminum elements and its availability for absorption by the plant decreases. The supply of P needed by plants is mainly achieved through chemical fertilizers; however, in addition to the high price of these fertilizers, in the long run, their destructive effects will affect the soil and the environment. The use of cheap and abundant resources such as rock phosphate (RP) can be an alternative strategy for P chemical fertilizers, but the solubilization of P of this source has been a challenge for agricultural researchers. For this, physical and chemical treatments have been used, but the solution that has recently attracted the attention of the researchers is to use the potential of rhizobacteria to solubilize RP and supply P to plants by this method. These microorganisms, *via.* mechanisms such as proton secretion, organic and mineral acid production, siderophore production, etc., lead to the solubilization of RP, and by releasing its P, they improve the quantitative and qualitative performance of agricultural products. In this review, addressing the potential of rhizosphere microbes (with a focus on rhizobacteria) as an eco-friendly strategy for RP solubilization, along with physical and chemical solutions, has been attempted.

Keywords: rock phosphate; phosphate solubilizing bacteria; organic acids; siderophore

1. Introduction

Indiscriminate consumption of phosphate fertilizers, in addition to high costs of importing fertilizers from abroad, also has harmful effects. Among these effects, the following can be pointed out: phosphorus poisoning caused by excessive absorption, increasing its concentration in plant tissues, and disrupting the balance of nutritional elements; accumulation of boron in the plant to the extent of toxicity; reducing the absorption of copper;

immobilizing iron in the soil and preventing its absorption by the root; disrupting the metabolism of zinc in the plant; reducing mycorrhization of the root; soil contamination with cadmium; decreasing the yield and quality of the product; increasing the negative charge of soil and water pollution to phosphorus and occurrence of the eutrophication phenomenon; etc. [1–4]. For this reason, today, agricultural operations have moved towards more sustainable and environmentally friendly approaches. Considering the problems mentioned for the use of chemical fertilizers [4], the importance of alternative options becomes more apparent. One of the alternative solutions is to use cheap and accessible sources of phosphate. One of the most important sources is rock phosphate (RP) [5].

RP is a natural, abundant, and cheap source of phosphate. Due to the low absorbability of phosphorus in this source, as well as several reasons such as the calcareous nature of most soils, the presence of high pH, drought stress, the presence of a lot of bicarbonate in irrigation water, and the lack of organic matter in agricultural soils, the direct use of this source is not common in soils (especially in calcareous soils) [4–6]. However, the results of the research conducted by different researchers have shown that it is possible to increase the absorption capacity of phosphorus in the RP source through a number of strategies and make it a substitute for part of the phosphorus fertilizers used in agriculture [6].

There are many solutions including physical, chemical, and biological methods to increase the reactivity of RP and its soluble phosphorus, which increase its usability [7]. In the physical method, by mixing RP and soluble phosphate fertilizers or by reducing the size of its particles [8], in the chemical method by completely or partially acidifying the RP [9], and in the biological method by using different microorganisms [10,11], the available phosphorus of RP can be increased. Phosphate solubilizing microorganisms (PSMs) are a group of useful microorganisms that are able to convert insoluble inorganic and organic phosphorus compounds into soluble forms [12,13]. Among these microorganisms, bacteria are one of the most important. Among the bacterial genera, *Bacillus*, *Pseudomonas*, and *Rhizobium* are very significant and important [14].

According to the information mentioned above, the continuous and long-term use of phosphorus chemical fertilizers, in addition to high costs, will cause irreparable damage to the health of the soil and the environment, and ultimately to humans, and the use of alternative solutions to supply phosphorus needed by plants in an eco-friendly way is felt more than ever. The use of RP along with its solubilizing microbes, especially bacteria, is one of the strategies that has recently attracted the attention of the world's agricultural scientists; therefore, in this review, various dimensions of this issue, such as the types, characteristics, and effective factors of soil in dissolution of RP, as well as different strategies for treating RP and increasing its solubilization, and finally the results of applied research on the use of RP with solubilizing microbes, especially rhizobacteria, and solubilization mechanisms, have been discussed.

2. Phosphorus

In many soils, the second-highest vital macronutrient, phosphorus (P), is essential for higher and sustained production from agriculture [15]. It is necessary for the transmission and conservation of energy in organisms via ATP (adenosine triphosphate) and aids in the synthesis and stability of DNA and RNA. Similar to the way that adequate P nutrition is required for the structural as well as functional reliability of cell membranes, P is a fundamental element of membrane phospholipids [16]. The primary component of cell membranes, phospholipids, is necessary for their durability and function, as well as having an impact on cell membrane transport pathways. It is possible to anticipate structural defects in cellular membranes under P deficits, which will hurt nutrient transfer across the root cellular membranes. P is crucial in every way, from a molecular perspective to numerous physiological and also biochemical methods: for example, photosynthesis [17], stalk in addition to stem strength, cell division and enlargement, flower and seed development, root growth, root development, production of energy, storage, transport reactions, crop maturity and quality, N fixation in legumes, and disease resistance [18].

2.1. Phosphorus in Soil and Soil Solutions

P enters the earth from both organic and inorganic sources through a variety of processes, including mineralization, immobilization, adsorption, precipitation, desorption, weathering, and decomposition. It may also enter the soil via compost, dead plant material, or animal debris [19]. Because it is an active element, the soil does not contain P in its elemental state. With total P concentrations typically falling between 500 and 800 mg/kg dry soil, it almost solely takes the form of orthophosphate in soil. Only a small percentage of the macronutrient P is water soluble, resulting in its being the minimum accessible element in soil when compared to the rest of the macronutrients [20]. A significant component of this P is linked to an organic component, and in soils rich in minerals, the total organic P ranges from 20 to 80% of the total P [3]. P in the soil solution is completely accessible despite making up a small portion of the overall soil P. However, the concentration of P that is soluble in soil solutions is usually very low, ranging from ppb in severely deficient soils to 1 mg/L in the soils where the consumption of phosphorus fertilizer is high [18,21]. Above 90% of the total sum of P exists in fixed and insoluble forms, non-labile fractions such as primary phosphate (*Pi*) minerals, humus-P, P-bonded Ca, Fe, and Al, and P immobilized by hydrous oxides and silicate minerals. It has been reported that the rate of P fixation in Alfisols, Inceptisols, Vertisols, Entisols, and Aridisols was 88.68%, 68.73%, 66.84%, 68.33%, and 58.24%, respectively. The higher rate of P fixation in Alfisols has been attributed to sesquioxides [22]. In light of the findings of multiple regression studies, the ability of soil to fix phosphorus relies to an extent on the soil's pH, active iron, organic carbon content, and clay content. While in the labile portion, solid phosphate remains trapped on soil surfaces and can be found in phosphate precipitations. P availability is affected by a number of soil factors, such as soil texture, pH, the microbial activity, and the presence of cations such as calcium, iron, and aluminum [23].

2.2. Phosphorus Availability to Plants

In plants, P takes up between 0.1% and 0.5% of dry weight, and it constantly exists in ortho- and pyrophosphate, two of its greatest oxidation states [24]. The majority of Pi fertilizer is leached into the ecosystem, with negative effects such as soil degradation and water eutrophication [2]. Plants only take up 15–25% of the available nutrients [24]. Soil P supply for a plant is heavily influenced by its P acquisition strategy. Plants lacking in phosphorus exhibited a variety of signs. Several plants form the first signs of P shortage including discoloration of the leaves, which results in blue-green foliage. The leaf's purple color results from the buildup of sugars, which boosts the production of the purple pigment anthocyanin [25]. A lack of P can also affect the quantity, viability, and growth of seeds [26]. Plants themselves exhibit a variety of physiological and root structural modifications in response to a P deficit [27], making it challenging to determine the relative significance of processes mediated by microbes versus plants for P mobilization. The maintenance of rising soil P levels is an important task for agricultural scientists, ecological researchers, and farm managers because plants only take up P in a soluble state, while most P in soil is insoluble [28]. To overcome these restrictions, many artificial P-fertilizers have been used since the 1960s. However, 75 and 90% of this additional P fertilizer is coagulated by Fe, Ca, and Al compounds that are already found in the soil [29], rendering it inaccessible to plants. The use of soil microbes with a capacity to solubilize P is therefore important to highlight and these may be used as inoculants for distributing P from limited sources in soil [12,13,30].

3. Rock Phosphate (RP)

RP is a general term for a collection of different minerals in which the concentration and amount of phosphate is significant and high [31]. RPs are natural substances that contain about 5 to 13% phosphorus and are found in nature mainly in igneous and sedimentary forms. About 13–15% of RPs are igneous, 80–82% are sedimentary, and only 2–3% are biogenic sources [5]. RP is mainly from apatite type, which can be extracted commercially and used directly or after processing for use in industry or agriculture [32]. Many studies have shown that the application of RP has not had an acceptable effect on plants due to low solubility [33] and soil conditions [34]. RPs usually exist in most climates of the world, although they are mostly seen in tropical and subtropical climates [35]. RP exists in sufficient quantities in some regions of the world such as Europe and India, but some countries such as Australia are completely dependent on its import [36]. The global production of RP in 2012 was reported to be 217 million tons and global reserves were about 67 billion tons [37]. With the increase in population, researchers estimate that the existing reserves may be unable to meet the global demand for phosphate rock in another 100 years [38]. Most unprocessed RPs are usually unusable because their solubility is very low [39].

3.1. Types

Although the term RP is universally accepted, any natural geological material containing one or more phosphate minerals may not be suitable for commercial processing [37]. There are five types of RP in the world, which include marine phosphate deposits, igneous deposits, metamorphic deposits, biogenic deposits, and weathered phosphate deposits. About 75% of them are marine sediments, 15–20% are weathered igneous, and only 1–2% are biogenic, from the accumulation of droppings of birds and chickens [40]. The most common and widespread RPs (87%) are of sedimentary and marine origin (37). The RPs of Russia, Brazil, and South Africa are igneous; the RPs of North Africa, Jordan, and Florida are sedimentary; and the RPs of India are metamorphic [41]. Apatite is found in almost all igneous RPs and its amount is between 0.1 and 1%. Apatite and feldspars are the most dominant minerals forming RP, which are almost equal in weight and the amount of P_2O_5 in them is between 50 and 90% [42].

3.2. Characteristics

The chemical composition of RPs of different countries has shown that they have essential elements, rare elements, metals and semi-metals, radionuclides, and rare earth elements [35]. The essential elements of RP include primary macro elements (phosphorus), secondary elements (calcium and magnesium), and micro elements (Fe, Mn, Zn, Cu, B, and Mo). Considering that the lack of phosphorus is the main limitation of agricultural production, phosphorus in RP is one of the most important elements in agriculture [43]. Sedimentary RPs usually have 30–35% and igneous RPs often have less than 5% P_2O_5, but their phosphorus can be concentrated and increased to about 35 to 40% or even more [44]. The amount of phosphorus in the world's important RPs is given in Table 1. The amount of P_2O_5 in RPs of most countries is about 30%, except for Russia, which is 15%. The amount of calcium in RPs of Morocco, Tunisia, Jordan, East Africa, Senegal, Togo, and Nigeria is about 50%. Brazilian RP has the highest amount of magnesium (12.7%) and Senegal's RP has the lowest amount. The amount of magnesium in the RPs of China, Morocco, East Africa, Nigeria, and Tunisia is slightly more than 1% (Table 1).

Table 1. The percentage of essential elements and minerals in RP [7].

Type of Minerals	MgO (%)	CaO (%)	P_2O_5 (%)	Country
A, Q	0.37	48	29–33	America
A, C, D, F, M	0.95–3.93	31–35	19–36	China
A, D	0.27–2.24	44–52	27–33	Morocco
A, Q, M	0.32	24.7	15	Russia
A, C, D, Q	0.45–1.28	47–50	29–30	Tunisia
A, C, Q	0.23–0.3	47–50	30–32	Jordan
A, Q, K, M	0.21–12.7	27–31	18–37	Brazil
A	0.44–1.5	52–54	36–40	East Africa
A, C, Q	0.06	50.1	35.5	Senegal
A, Q, K	0.1–0.29	39–50	28–36	Togo
A, C, Q	0.11–0.35	14–52	11–36	Nigeria

Note: A: apatite; C: calcite; D: dolomite; F: feldspar; K: kaolinite; M: mika; Q: quartz.

4. Effective Factors in Increasing the Solubility of RP

4.1. Reactivity of RP

The reactivity of RP is a measure of the amount of dissolution of it in standard laboratory conditions (in a specific soil or in special agricultural conditions). In this definition, the changes made in the dissolution rate of RP by different soil characteristics and plant effect are not included, and the chemical composition and particle size of RP determine their reactivity [45]. RPs of sedimentary origin are usually the most reactive and therefore suitable for direct application [46]. The chemical characteristics that affect the reactivity of RP include the crystal structure of phosphate (apatite) and the presence of accompanying minerals, especially calcium carbonate. Increasing the substitution of carbonate instead of phosphate in the crystal structure usually increases the reactivity of RP. This substitution plays a role in changing the cell dimensions and also in weakening the crystal structure of apatite [47]. RPs in which the molar ratio of phosphate to carbonate is 3 to 3.5 have the highest reactivity.

Calcium carbonate is one of the most common minerals in RP. The dissolution of calcium carbonate increases the concentration of calcium and pH; therefore, it will not be surprising that calcium carbonate can reduce the dissolution rate of RP in some soils [48]. In field conditions, leaching and plant absorption may decrease calcium ions. The amount of reduction of ions by washing varies according to the type of soil, climatic conditions, and the method of using RP. In other words, the presence of more than 13% of free calcium carbonate may reduce the effectiveness of RP in the soil [49].

For agricultural effectiveness, a certain RP should not only be dissolved, but the dissolved RP should be absorbable by the plant. Soil characteristics including low pH (less than 5.5), low concentration of soluble calcium ions, low amount of absorbable phosphorus in agricultural soil, and high amount of organic matter increase the dissolution of RP [50].

4.2. Soil pH

The dissolution of RP may be expressed in the form of the following equation:

$$Ca_{10}\,(PO_4)_6F_2 + 12H_2O \rightarrow 10Ca^{2+} + 6H_2PO_4{}^{-} + 2F^{-} + 12OH^{-}$$

Although the above reaction is written for fluorapatite RP, it can be used for other apatite minerals including reactive RP. As the above reaction shows, the result of RP dissolution is the release of hydroxyl ions into the soil solution. The neutralization of hydroxyl ions (OH^-) released by the soil causes the dissolution of RP to continue. In the case that phosphate is replaced by carbonate in RP, more hydrogen ions will be needed to neutralize the hydroxyl ions formed by the release of carbonate ions into the soil solution [51,52]. Each carbonate ion is connected to two hydrogen ions and forms a molecule of water and carbon dioxide gas; therefore, the presence of many hydrogen ions is very important for the continuous dissolution of RP.

4.3. Concentration of Available Phosphorus in Soil

Because the concentration of phosphorus in the soil solution is very low (0.05 to 0.5 mg/L), it has little effect on the dissolution of RP [44,47]. However, there are reports that as the phosphorus absorption capacity of soils increases, the discharge of soil soluble phosphorus increases and the dissolution of RP is increased [53]. When a small amount of RP is added to soils with severe phosphorus deficiency, these soils strongly absorb almost all dissolved phosphorus, and the amount of dissolved phosphorus increases very little. This action causes a very small increase in crop production (Zone A, Figure 1). In a large amount of added phosphorus, because the dissolved phosphorus reaches above the threshold (critical) concentration for the net absorption of phosphorus by plants, the crop production increases strongly (Zone B, Figure 1) [54]. Soils with moderate phosphorus content are likely to be effective at the starting point of Zone B. In this case, the dissolved RP is probably absorbed by the plant; therefore, the soils should preferably have medium to high phosphorus content to obtain a suitable performance from increasing RP with a constant dissolution rate. The rate of constant dissolution is equivalent to the amount of phosphorus absorbed by the plant. In such soils, plant-absorbable phosphorus can act as a phosphorus starter fertilizer for the germination and initial growth of the plant, which, as a result, helps in root growth and more and more effective use of RP [55]. This situation is similar to the effect of phosphorus dissolved in water on the effectiveness of RP. Zone C in Figure 1 shows that increasing RP has no effect on increasing plant yield.

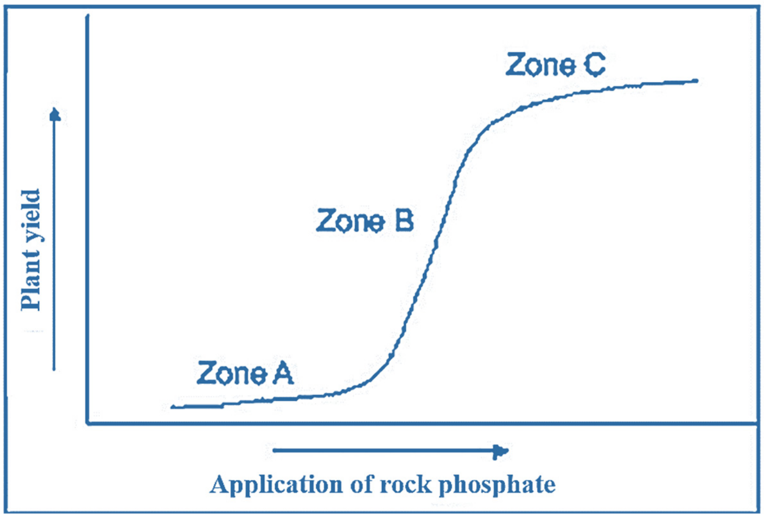

Figure 1. Schematic pattern of the plant response curve to the addition of RP in soil with severe phosphorus deficiency [54].

4.4. Soil Organic Matter

Among the other characteristics of the soil that increase the dissolution of RP and its ability to be absorbed by the plant is the organic matter of the soil. The reasons for the increase in dissolution include the high cation exchange capacity of soil organic matter, the formation of calcium-organic matter complex, the dissolution of RP by organic acids, and the blocking of phosphorus absorption sites in the soil [50]. The cation exchange capacity (CEC) of soil organic matter is higher than that of clay minerals. Based on the amount of soil clay, the CEC of mineral soils may range from very low to 24 meq/100 g, while in organic matter, this value may reach more than 200 cmolc/kg [56]. Increasing the CEC of soil organic matter increases the calcium absorption capacity of soils and therefore causes more dissolution of RP. The parts of humic acid and fulvic acid of organic matter form a complex with calcium, which reduces the concentration of dissolved calcium and, as a result, increases the dissolution of RP [57].

4.5. Climatic Conditions

Rainfall is one of the climatic factors that is effective in the dissolution of RP and its agricultural effectiveness. Increasing soil water by rainfall or irrigation increases the dissolution of RP. The reason is the increase in the rate of neutralization of the released OH^- ions and the displacement of calcium and other reaction products near the surface of RP particles. Sufficient water supply stimulates plant growth and increases phosphorus absorption by the plant, thereby increasing the agricultural effectiveness of RP. Of course, the required amount of rainfall depends on the characteristics of the soil. Studies have shown that the temperature of 5 to 35 degrees Celsius has a very minor effect on the solubility of RP and has a very small effect on their agricultural effectiveness [8].

4.6. Plant Species

Different species of plants have different phosphorus absorption capacities, amounts, and patterns of phosphorus absorption [58]. In addition, different plants have different absorption power in absorbing phosphorus from less soluble or non-absorbable forms [59]. Among them, some plants can dissolve RP and absorb the reaction products [60]. Permanent pastures, trees, and seedlings need a constant supply of phosphorus during the growth period, and, considering that RP dissolves in the soil gradually and provides phosphorus at a constant rate, using RP is beneficial for these plants [61]. Legumes are also suitable plants for using RP. Due to their ability to absorb a lot of dissolution reaction products (high need for calcium) by acidifying the soil adjacent to the root system (rhizosphere), they are effective in the dissolution of RP [62]. This effect can play a role in improving phosphorus nutrition of accompanying plants (mixed cropping) or for subsequent plants that alternate with legumes [63]. Some species of plants (such as rapeseed and Egyptian bean) have been studied due to their ability to secrete organic acids that increase the dissolution of RP [64]. Studies have shown that reactive RPs may be used, even in alkaline soils along with plants that secrete organic acids such as rapeseed [33].

5. Strategies to Increase Dissolution of RP

5.1. Physical Methods

5.1.1. Reducing the Size of RP Particles

Reducing RP particles to nanoscale and thus increasing the total surface area can create a physical mechanism to increase the efficiency of RP and create more effective phosphorus fertilizer [65]. The researchers stated that the use of 1000 kg/ha of RP nanoparticles, in addition to increasing soil pH, improved the growth indicators of spinach plants in an acidic soil [66].

5.1.2. Mixing RP with Phosphate Fertilizers

Fertilizers that are similar to the chemical composition of partially acidified RP can be indirectly prepared by enriching dry RP with soluble phosphate fertilizers such as simple superphosphate and triple superphosphate under high pressure. The production of these fertilizers, in addition to costing a lot of energy, also causes many environmental problems [67]. The amount of soluble phosphorus of this type of fertilizer depends on the ratio of RP to the used water-soluble phosphorus fertilizer. This technology (enrichment) is usually used for RPs, which are not suitable for partial acidification due to having a lot of sesquioxides of iron and aluminum. The results showed that the effectiveness of RP (even if its reactivity is low) increased after enrichment and then the water-soluble phosphorus also increased. Under these conditions, the enrichment of RP with water-soluble phosphate fertilizers with a ratio of 50:50 increases the agricultural and economic effectiveness of igneous RP in developing countries. However, the agricultural effectiveness of the rich fertilizers produced compared to the water-soluble phosphorus fertilizers depends on a number of factors mentioned in the partially acidic RP [68]. During the field experiments, Missouri RP and simple superphosphate were prepared in a ratio of 2.2:1 and added to the soil at three fertilizer levels. The results showed that in an alkaline soil (pH = 8.2), the RP-simple superphosphate mixture was as effective as simple superphosphate. In addition, it was economically similar to simple superphosphate based on three-plant rotation. Observations have shown that the dissolution of RP when mixed with simple superphosphate has increased by about 55% compared to the use of RP alone [69].

5.2. Chemical Methods

The dissolution of RP can be performed in two main ways, i.e., partial acidification and complete acidification. Both paths can be done by organic or inorganic acids. Chemical methods to increase the effectiveness of RP include partial acidification of RP. Partially acidified RP is prepared by reacting RP with sulfuric acid and phosphoric acid in a lower amount than what is needed to make simple and triple superphosphate [7,70]. Partial acidification RP is a cost-effective way to improve the ability to supply phosphorus to native soils that have low solubility by nature [70]. The partial dissolution of RPs is based on the acidification of one-third of phosphate materials by acids to produce soluble monocalcium phosphate, which is known as superphosphate in the fertilizer industry [71]. Since Nordengren [72] first reported the use of partially acidified RP, this RP has been widely used in Europe and South America. Partially acidified RP is an economic method to increase the agricultural effectiveness of igneous RP resources, which are otherwise not suitable for direct use. For this reason, comprehensive studies have been conducted at the international level [8,33]. Partially acidified RP is cheaper compared to water-soluble phosphate fertilizers due to reduced consumption of acid and energy per unit of phosphorus production, in addition, the amount of phosphorus in partially acidified RP is often higher than that of simple superphosphate [9]. One of the new technologies developed recently is the activation of phosphorus in dolomite RP to convert dolomite into slow-release fertilizers [48,73]. The results of greenhouse studies showed that the use of activated dolomite phosphate could continuously provide the phosphorus required by the plant during plant growth [46]. Ahmad et al. [74] reported that the use of RP activated with oxalic acid reduced the absorbable form of lead and copper, which can be due to the increase of absorbable phosphorus and the increase of pH. The agricultural effectiveness of partially acidified RPs is different and depends on the following factors: 1—Physical and chemical characteristics of the RP used. 2—Degree of acidification. 3—Chemical characteristics of the soil, especially pH and absorption (retention) of soil phosphorus. 4—Cultivation systems [7,71].

5.3. Biological Methods

5.3.1. Mixing RP with Organic Matter

Among the effective approaches of increasing crop yield in the direction of sustainable agriculture is the use of organic fertilizers [75]. Organic matter is the key to soil fertility. To maintain the fertility level and production power of a soil, the amount of organic matter must be maintained at an appropriate level. Most of the soils have unfavorable physical and chemical properties due to the low or lack of organic matter, and this causes insufficient plant growth and low yield in these soils. In order to increase soil fertility and productivity, the use of organic fertilizers such as animal manure, green manure, and vermicompost are very important [76,77]. Studies have shown that the use of cow manure increased the seed yield of agricultural plants and soil organic carbon and nitrogen and improved soil properties including electrical conductivity and pH [78,79]. In addition, organic matter improves soil porosity, increases soil aeration, and can reduce the deficiencies in sandy soils in water retention and reduce the severity of tuberculosis in clay soils [80]. Organic matter accelerates the growth of microorganisms in the soil and could be useful for them in various aspects. It can also store the nutrients needed by the plant and release it when needed for plant absorption [81]. Adding animal manure or compost and green manure or any other type of organic material to the soil increases the ability of the soil to absorb phosphorus (Figure 2). Submerging animal and green manures and adding any organic matter to the soil increases the ability of plants to absorb phosphorus; the use of organic fertilizers, in addition to increasing the population of beneficial organisms, usually causes a decrease in harmful organisms such as pathogens and plant pests [82].

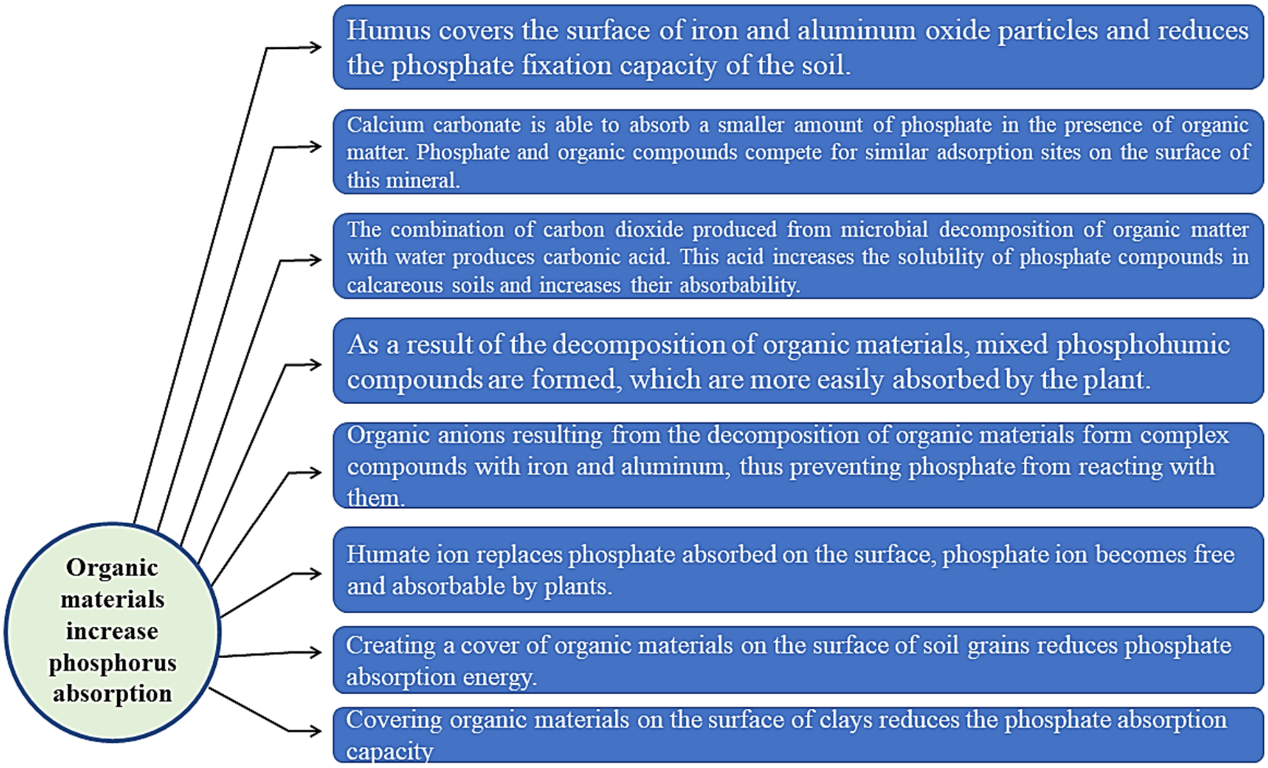

Figure 2. Organic matters increase phosphorus absorption in different ways [83–85].

5.3.2. Phosphate Solubilizing Microbes (PSMs) in P Availability

Phosphate solubilizing microbes (PSMs), a class of microbes that can solubilize the fixed molecules of both inorganic and organic P, can enhance the accessibility of P to crops [86]. The quantity of soluble Pi available could be increased by PSMs. By enhancing the effectiveness of biological nitrogen fixation, increasing the accessibility along with crop uptake of additional trace elements such as Zn, Fe, etc., or producing regulators that promote plant development, their activity promotes the growth of plants. The majority of PSMs were discovered in various plants rhizospheres, where they have been found to have greater biochemical activity [21,87].

- Bacteria

Insoluble Pi can be more easily dissolved by bacteria than by fungi [10]. Phosphate solubilizing bacteria (PSB) account for 1–50% of the total number of the various microorganisms [11]. Among the various bacterial groups, endo-symbiotic rhizobia and ecto-rhizospheric strains of *Pseudomonas* and *Bacillus* were identified and characterized as efficient phosphate solubilizers [11–13]. Numerous PSBs from a range of communities have been detected, including *Pseudomonas*, *Erwinia*, *Bacillus*, *Serratia*, *Micrococcus*, *Flavobacterium*, *Enterobacter*, *Agrobacterium*, *Bradyrhizobium*, *Azotobacter*, *Salmonella*, *Escherichia coli*, *Arthrobacter*, *Alcaligenes*, *Chromobacterium*, *Streptomyces*, and *Thiobacillus* [88]. The strongest P solubilizers are populations from the bacterial families *Pseudomonas*, *Rhizobium*, *Enterobacter*, and *Bacillus* [89]. Studies indicate that PSBs, such as *P. putida*, *P. fluorescence*, etc., when combined with RP and single superphosphate (SSP), can decrease the P dose by 25–50%. As biofertilizers, the use of bacterial inoculants promotes plant growth, P availability, and yield. They also produce phytohormones that encourage the development and growing of plant cells, which include gibberellins, cytokinins, and indole-3-acetic acid [11,13].

- Fungi

The second-most significant PSMs are fungi. As P solubilizers, they make up between 0.1 and 0.5% of the total microbial community. When subcultured repeatedly in a scientific setting, unlike bacteria, they retain their P-dissolving ability. Since fungi generate more acids than bacteria do, they are more active at solubilizing P. Because they can travel farther than bacteria in soil, fungi are more crucial for the P solubilization [90]. The largest number of groups of filamentous fungi that dissolve Pi are *Aspergillus* and *Penicillium* though isolates of *Trichoderma* and *Rhizoctonia solani* are also known to do so [91]. In addition, compounds can be solubilized by a nematofungus known as *Arthrobotrys oligospora*. The nematofungus *Arthrobotrys oligospora* has the ability to solubilize Pi both in vivo and in vitro [92]. A limited number of investigations on yeasts, including those on *Schizosaccharomyces pombe* and *Pichia fermentans*, have been conducted to establish the extent to which they can solubilize Pi [51]. As more research is done, a greater variety of Pi-solubilizing filamentous fungi should be characterized. Many of those present have been found to increase the development of plants by 5–20% after inoculation, such as *Aspergillus* sp., *Penicillium* sp., and *Mucor* sp., which are frequently found in agricultural soils [93].

- Arbuscular Mycorrhizal Fungi (AMF)

Along with bacteria, fungi, and actinomycetes, mycorrhiza was also discovered to have P solubilizing action. The crop species forms root groups that are efficient at absorbing P by releasing root exudates such as organic anions, phenolic acids, protons, and enzymes in the presence of extremely low soil P availability [90,94]. Phosphate mineralization, being derived from both organic and inorganic elements, is significantly aided by the application of AMF and plant growth-promoting microorganisms (PGPM). The AMFs *Entrophospora colombiana* and *Glomus manihotis* are the components of the microbial inoculum. When phosphatic bio-fertilizers such as PSMs are utilized, the solubility of the natural and applied Pi increases. In acidic, low-Pi soil, rhizobacteria and AMF interacted to affect the development and nutrient intake of *Sorghum bicolor* [90,95].

- Actinomycetes or Actinobacteria

Actinomycetes or Actinobacteria have the ability to solubilize P, which has recently attracted interest because these microbial organisms have other potential uses (which include the synthesis of antibiotics as well as phytohormones that might concurrently help plant development) in addition to their capacity to live in harsh environments [30,96,97]. According to research by Hamdali et al. [30,96], P can be solubilized by 20% of actinomycetes, which includes members of the common species *Micromonospora* and *Streptomyces* [30].

6. Mechanism of PSMs in the Release of Unavailable P

Different strategies are used by PSMs to render phosphorus available for plants to absorb. Lowering soil pH, chelation, and mineralization are among the most important of these.

6.1. Lowering Soil pH

Phosphorus is capable of precipitating in alkaline soils to create calcium phosphates, such as RP, which might be inaccessible in the soil. PSMs release organic acids that lower soil pH and improve permeability [98]. In alkaline soil, P forms bivalent as well as trivalent forms of inorganic P. Organic acids are by-products of microbial fermentation produced by oxidative respiration, while glucose is used as a source of carbon [98]. Various organisms release various types and amounts of organic acids. Alam et al. [99] stated that the secretion of organic acids and the solubilization index have a significant positive relationship.

6.2. Chelation

The inorganic as well as organic acids generated through PSM compete with Pi for binding sites in the soil by breaking down inorganic soil Pi by chelating cations [100]. The carboxyl and hydroxyl groups of the acids chelate the cations attached to Pi, resulting in their being soluble. These acids, which react with insoluble Al and Fe oxides to stabilize them, may complete fixation sites. The calcium chelator 2-ketogluconic acid has an abundance of strength [21]. Manufacturing of inorganic acids, including nitric [12], carbonic acid [101], and sulfuric [86], is being identified. Calcium phosphate reacts with nitric and sulfuric acids to transform into soluble forms [86]. Additionally, di- and tricarboxylic acids have been shown to function better than monobasic and aromatic acids, and aliphatic acids outperform phenolic, citric, and fumaric acids in terms of their ability to dissolve Pi. [102]. Citric, succinic, lactic, 2-keto gluconic, gluconic, glycolic, malic, oxalic, fumaric, tartaric, propionic, adipic, glutaric, butyric, malonic, and glyoxylic acids are the most common organic acids that solubilize phosphates [87]. Among these, gluconic acid as well as 2-keto gluconic acid appear to be the most typical solubilizers of the mineral Pi. [98]. According to reports, PSB such as *Burkholderia cepacia* and *Pseudomonas* sp. generate gluconic acid as their main organic acid. Furthermore, 2-ketogluconic acid, which is discovered in isolates of *Rhizobium meliloti*, *Bacillus firmus*, and *Rhizobium leguminosarum*, is yet another organic acid found in isolates with the capacity to dissolve Pi [101]. Lactic, acetic acid, isobutyric, and isovaleric combinations were discovered to be produced by *Bacillus licheniformis* and *Bacillus amyloliquefaciens* strains. It has been proposed that Gram-negative bacteria are superior to Gram-positive bacteria at breaking down mineral phosphates because numerous kinds of organic acids are released into the surrounding soil [21]. PSMs are also known to produce acidity by generating CO2, as revealed by the dissolution of calcium phosphates [103].

6.3. Mineralization

Mineralization and soil organic matter that binds P is essential for the agricultural land's P cycling. PSMs create phosphatases such as phytase, which hydrolyze various organic Pi molecules and liberate inorganic P, which will be immobilized by plants, mineralizing organic P from the soil [104]. Phytase-producing fungi that are frequently documented include the following: *Penicillium simplicissimum*, *Aspergillus candidus*, *Aspergillus niger*, *Aspergillus parasiticus*, *Trichoderma viride*, *Aspergillus terreus*, and *Trichoderma harzianum* [105,106]. The concentration of C:P in the soil-deposited residues determines the amount of P mineralization over immobilization [107]. If the organic matter's C: P ratio is less than 200:1, mineralization happens quickly. If it is greater than 300:1, immobilization is going to be the main process [108]. Through the creation of extracellular enzymes, such as phytases phospholipases, and phosphodiesterases, soil bacteria such as *Bacillus* and *Streptomyces* spp. are capable of mineralizing complicated organic phosphates. [21]. Yi et al. evaluated the functions of exopolysaccharide (EPS) during the dissolution of P using four bacterial strains: *Enterobacter* sp. (EnHy-402), *Arthrobacter* sp. (ArHy-505), *Enterobacter* sp. (EnHy-401), and *Azotobacter* sp. (AzHy-510). These strains can solubilize TCP (tricalcium phosphate) [109]. These PSB showed an effective capacity for P-solubilization and generated a significant amount of EPS. To fully comprehend the connection between the creation of EPS and the solubilization of Pi, however, more research is required. Similar to this, some PSMs produce siderophores and degrade organic soil P, boosting the available P [98,110]. The various groups of pyrroloquinoline quinine (pqq A–F), enolase (eno), and glucose dehydrogenase (gcd) genes regulate all of the abovementioned mechanisms of Pi solubilization [111].

7. Factors Affecting the Solubilization Mechanism of RP by PSMs

Soil conditions can affect the ability of soil microbes to solubilize phosphate from insoluble sources such as RP. In some conditions, such as nutrient-deficient soils, high-temperature soils, saline-alkaline soils, etc., the tendency of microbes to solubilize phosphate has increased compared to normal conditions [112]. Regarding the effect of temperature on the mechanism of phosphate dissolution, there are various reports such as the optimal temperature of 20–25 °C [113], 28 °C [114], and 30 °C [115]. Additionally, the ability of phosphate solubilization by soil microbes has been reported at extreme temperature of 45 °C in desert soil [116,117] and at low temperature of 10 °C [118]. Some other factors influencing the activity of phosphate solubilization by soil microbes are the climatic conditions of the region [119], the presence or absence of vegetation, the growth stage of vegetation [120], other soil microbes [116], agricultural practices, land use systems [120], and physical and chemical characteristics of soil [116] such as pH, amount of soil organic matter, etc. [121]. It has been reported that well-aerated soil is more favorable for phosphate solubilization activity compared to water-saturated soil [122].

8. The Results of Using RP with PSMs in Agriculture

Xu et al. [123] investigated the effect of using phosphate solubilizing bacteria (PSB) and RP on reducing Pb^{2+} mobility and increasing phosphorus in lettuce. The results showed that *Bacillus thuringiensis* strain GL-1 and *Pantoea anathosis* strain HCR2 bacteria can effectively dissolve RP and release its phosphorus by producing citric, gluconic, and alpha-keto-glutaric acids. The results of the measurement in the culture medium showed that phosphorus solubilized by PSB quickly reacted with Pb^{2+} and formed insoluble Pb^{2+} compounds, which was confirmed by electronic microscope scanning and X-ray diffraction devices. In the pot experiment, the use of PSB and RP increased phosphorus absorption, and the biomass of aerial organs and the net photosynthesis rate of lettuce plants increased significantly, while the plant absorption of Pb, Zn, and Cd elements significantly decreased. The results of this research showed that the use of RP along with PSB can be effective in reducing the consumption of chemical fertilizers and can be used in the field of soil remediation from heavy metals. Barazetti et al. [124] investigated the effect of using RP, vermiculite, and peat as a mycorrhizal fungus (MF) carrier in increasing the growth indicators of corn and soybean plants in laboratory and field conditions. The results showed that in soybean plant, MF inoculation based on phosphate carrier caused a significant increase in nitrogen and phosphorus in the leaves. In corn plants, the use of RP carrier along with MF increased the amount of phosphorus and nitrogen in leaves. de Amarel Leite et al. [125] reported that the combined use of PSB and RP increased the dry weight of the shoot part and phosphorus of corn plants. Khan et al. [126] reported that the use of RP + compost + sulfur + *Thiobacillus* bacteria increases the yield of the whole plant, seed yield, stem yield, plant height, thousand seed weight, spike length, number of seeds per spike, absorption of nitrogen, phosphorus, zinc, copper, iron, and manganese nutrients of wheat plant. Additionally, the use of these treatments increased soil organic carbon, soil absorbable phosphorus, and total soil nitrogen. The basic principle in the combined use of elemental sulfur and RP is that when this complex is added to the soil, the native inoculated population of bacteria oxidizes the sulfur to sulfuric acid. Then this acid reacts with the particles of RP that are present in the vicinity of sulfur and forms monocalcium phosphate and dicalcium phosphate. Therefore, the dissolution of RP in the soil is intensified by local acidification and also causes partial soil acidification. *Thiobacillus thioparus* and *Thiobacillus thiooxidans* species are important sulfur oxidizing bacteria. Inoculating *Thiobacillus*-rich soils may not be necessary, but their inoculation increases the dissolution rate of RP after adding to the soil. Biswas et al. [127] used low grade rock phosphates (LGRP) as an alternative phosphorus source for wheat growth in an Inseptsol soil. They used PSB to inoculate LGRP in in vitro and pot experiments and compared its efficiency with chemical phosphate fertilizer. They hypothesized that PSB inoculation increases P solubility from LGRP and reduces P fixation in soil, thus improving the P supply parameter and increasing P availability to plants. The results of the in vitro experiment showed that LGRP inoculated with PSB could provide significantly more P compared to non-inoculated LGRP. Additionally, the potential of LGRP treatment inoculated with PSB for a better stability of P supply in the soil in the long term was shown. The pot experiment showed that combined application of LGRP inoculated with PSB + Diammonium Phosphate (DAP) can supplement 50% of phosphorus chemical fertilizer and maintain similar yield and P absorption compared to DAP treatment. In practice, PSB dissolved phosphorus from LGRP and soil, and also prevented phosphorus fixation in soil by mechanisms such as production of organic acids, siderophores, and phosphatase enzymes. Therefore, the application of LGRP inoculated with PSB provided a constant supply of available phosphorus to wheat during growth stages and coordinated the supply of this element with plant demand. The use of LGRP inoculated with PSB increased the amount of phosphorus absorption by 18% and reduced its fixation by 11%. According to the report of these researchers, the use of LGRP inoculated with PSB can be recommended in the production of crops to save phosphorus chemical fertilizer (about 50%) without loss of crop yield.

9. Conclusions

Considering the abundance and cheapness of RP, it can be processed by physical, chemical, and biological methods and used in soils (especially in calcareous soils). The more the pH of RP and soil decreases, the better the results of its application in soil will be. The use of sedimentary RP is better than igneous RP due to its higher solubility. The use of smaller sized RPs, mixing them with organic and inorganic acids, as well as the use of beneficial microorganisms such as phosphate solubilizing bacteria along with RP, gives more tangible results. The use of organic materials such as animal and poultry manure and humic and fulvic acid with low pH helps to dissolve it. Additionally, the use of plant species with the ability to produce different organic acids by plant roots in the use of RPs can also have better results. RP must be concentrated and processed by various physical, chemical, and biological methods before being used in plant cultivation; its direct use in the soil is not very effective. In addition, it is suggested that RPs be used in the activity area of plant roots together with phosphate solubilizing microorganisms.

Author Contributions: Conceptualization, D.M. and B.K.; writing—original draft preparation, B.K., D.M., A.F.N., M.C., M.P., Y.R.D., G.B., S.C., A.P., S.A. and S.S.; writing—review and editing, B.K., D.M., M.P. and S.C.; visualization, B.K.; supervision, B.E.G.-S., D.M. and B.K.; project administration, D.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: B.K. and A.F.N. are thankful to the Soil and Water Research Institute, Agricultural Research, Education and Extension Organization (AREEO), Karaj, Iran.

Conflicts of Interest: The authors declare no conflict of interest.

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