Review

Phosphorus Transformation in Soils Following Co-Application of Charcoal and Wood Ash

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Abstract: Phosphorus (P) is a vital soil macronutrient required by plants for optimum growth and development. However, its availability is limited because of fixation. The phosphorus fixation reaction is pH dependent. In acid soils, the predominance of aluminium (Al) and iron (Fe) oxides in both crystalline and amorphous forms reduces the solubility of soil inorganic P through fixation on positively charged surfaces and formation of insoluble Al and Fe precipitates. In alkaline soils, P readily reacts with calcium (Ca) to form sparingly soluble calcium phosphates. As a result, a large proportion of applied P may become chemically bound, whereas only a small fraction of soil P remains in the soil solution and available for plant uptake. To date, there is little information available on the use of charcoal with a highly negative charge and wood ash with high alkalinity to minimise P fixation in acid soils. Thus, this study examined the potential of the combined use of charcoal and wood ash to unlock P fixation in acid soils. Numerous studies have been conducted to identify effective approaches to improve P availability through the use of different types of soil amendments, regardless of whether P is organically or inorganically present. For example, to mitigate P fixation in acid soils, amendments such as compost and zeolite are used to reduce P sorption sites. These amendments have also been used to increase P uptake and crop productivity in P deficient acid soils by reducing soil acidity and the toxicity of Al and Fe. It is believed that long-term application of charcoal and sago bark ash can positively change the physical and chemical properties of soils. These improvements do not only reduce P fixation in acid soils, but they also promote an effective utilisation of nutrients through timely release of nutrients for maximum crop production.

Keywords: precipitation; adsorption; chelation; neutralising agent; porous structure; functional groups; organic acids

1. Introduction

Malaysian soils fall under the categories of either Ultisols or Oxisols [1], which together account for approximately 72% of the Malaysian land area [2]. These soils have pH values ranging from four to five, making them acidic in nature [3]. Ultisols and Oxisols are highly weathered because they occur in a tropical environment with high rainfall and temperature throughout the year [4]. Oxisols are the most highly weathered soils, but not necessarily the most acidic. This is because the increase in soil pH is related to the high point of zero charge (>pH 7) of aluminium (Al) and iron (Fe) oxides in the final weathering stage. Ultisols are less weathered but often more acid than Oxisols because they have typically significant amounts of silicate clay minerals (primarily kaolinite) [3]. In addition, these soils are inherently low in nitrogen (N), phosphorus (P), and potassium (K) [5], and their

cation exchange capacity (CEC) is low (<16 meq/100 g). Phosphorus becomes unavailable because it is fixed by sesquioxides in the soil system, leading to P deficiency in these soils [6]. As a result of this reaction, P is the most limiting nutrient in crop production. At a soil pH of below 5.5, P precipitates with both Al and Fe ions, whereas at a pH above 7, P precipitates with calcium (Ca) ions. Phosphorus availability is maximised at pH 6.5 for mineral soils and pH 5.5 for organic soils [7]. To reduce P fixation, farmers tend to apply large amounts of P fertiliser and lime to saturate Al and Fe ions and increase the soil pH [8]. However, this practice is uneconomical and environmentally unfriendly because excessive use of P fertilisers causes water pollution, such as in the form of eutrophication. In addition, over-liming leads to precipitation of P ions with Ca as calcium phosphate, which is not available for plant uptake.

Currently, the focus of researchers and farmers is shifting to the use of organic amendments, such as manures, composts, biochar, and agro-industrial waste [9,10]. Although some evidence on mitigating P sorption and fixation using organic matter exists [11–15], there is a dearth of information on the potential of using charcoal and wood ash to improve P availability. Charcoal has the potential to increase plant-available P because it has the ability to adsorb cations such as Al^{3+}, Fe^{3+} and Ca^{2+} that complex with P in the soil solution [16]. The highly porous structure of charcoal is resilient to biotic degradation, and this enables it to serve as a carbon-storage medium in ecosystems for a long time [17,18]. Furthermore, the abundance of pores in charcoal enables air retention, hence creating an aerobic condition in soils [19]. Demeyer et al. [20] reported that most wood ash has pH ranging from 8.9 to 13.5. Bramryd and Frashman [21] found that when wood ash was added to a soil, there was a decrease in acidity and Al ions. In addition, base saturation and microbial activities increase with decreasing soil acidity [22]. Moreover, using wood ash can increase water-holding capacity, moisture content, and nutrient availability because its hydrophilic property enables it to retain water [23]. Considering their physical, chemical, and biological properties, it is believed that the use of charcoal and wood ash to solve the problem of P fixation in acid soils may be novel. Therefore, the objectives of this study were to: provide an overview of the transformation and availability of P in soils; and discuss the possible mechanisms involved when charcoal and wood ash are used as P sinks in acid soils.

2. Soil Acidification

Soil acidification is defined as a decrease in acid-neutralising capacity (ANC) or an increase in base-neutralising capacity (BNC), resulting in an increase in acid strength as represented by the decrease in soil pH [24]. However, there is no clear threshold of which soils are considered acidic [25]. Different studies have established standards for the soil acidity level. Kochian et al. [26] stated that soils with a pH level of 5.5 or lower are considered to be acid soils. A clear-cut range of soil acidity was proposed by McFarland et al. [27] (Table 1). It is estimated that acidification has affected more than 1.5 billion hectares worldwide [28].

Table 1. Soil acidity range as proposed by McFarland et al. [27].

Level of Acidity	Soil pH
Slightly acid	6.6–6.1
Moderately acid	6.0–5.5
Strongly acid	5.5–5.1
Very strongly acid	5.0–4.5
Extremely acid	<4.4

Soil acidification occurs because of natural processes or anthropogenic activities. Natural acidification takes place in soils formed from acidic parent materials because leaching of minerals in such soils causes the loss of base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+). The base cations are then replaced by H^+ and Al^{3+}. In the tropics and subtropics, because the precipitation rate is higher than the evapotranspiration rate, leaching of base cations occurs

more effectively, resulting in accumulation of sesquioxides (oxides and hydroxides of Al and Fe) [29]. In addition, removal or harvesting of crops on agricultural lands causes rapid soil acidification [30]. During growth, crops absorb basic elements such as Ca, Mg, and K to satisfy their nutritional requirements. When these crops are harvested and the yield is removed from the field, the basic elements that are responsible for counteracting the acidity is lost, resulting in increased soil acidity. Increasing crop yields causes greater amounts of basic materials to be removed. Moreover, soil acidification is attributed to the extensive use of ammonium-based N fertilisers (NH_4) and urea-based fertilisers [($CO(NH_2)_2$)] [31]. Transformation of such sources of N fertilisers into nitrate (NO_3) via the nitrification reaction releases H^+ to increase soil acidity.

In addition, decomposition of organic matter causes soil acidity. Soil organic matter or humus has reactive carboxylic, enolic, and phenolic groups, and they serve as weak acids. During their dissociation they release H^+. Furthermore, the formation of carbon dioxide (CO_2) and organic acids during the decomposition also results in replacement of bases in the exchange complex with H^+. Carbonic acid (H_2CO_3) is formed when CO_2 from the atmosphere and root respiration dissolves in water [26]. In addition to carbonic acid, sulphuric acids can be generated in soils and contribute to soil acidification. Oxidation of two moles of sulphur during the decomposition of plant residues leads to the formation of two moles of sulphate ions ($SO_4{}^{2-}$) and four moles of H^+. In the soils of highly industrialised areas, acid rain is the main cause of soil acidification [32]. A chemical reaction occurs when sulphur dioxide and nitrogen oxides react with water, oxygen, and other chemicals in the atmosphere. As a result, they become sulphuric and nitric acids that mix with precipitation and fall to the ground. Precipitation is considered acidic when its pH level is below 5.2 [33].

Aluminium Phytotoxicity

Soil acidity is not only quantified by H^+ concentration, but it also by Al^{3+} concentration [34]. The concentration of Al^{3+} in solution increases exponentially as soil pH decreases below 5 [35]. This occurs because of the increase in hydronium ions (H_3O^+) in solution, which results in a rapid diffusion of protons into the soil's mineral structure and promotes hydrolysis [36]. Hydrolysis of Al increases H^+ in soils, thus increasing soil acidity. The chemical Equations (1)–(4) provide further explanation of the production of H^+ through hydrolysis of Al species.

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \tag{1}$$

$$Al(OH)^{2+} + H_2O \rightleftharpoons Al(OH)_2{}^+ + H^+ \tag{2}$$

$$Al(OH)_2{}^+ + H_2O \rightleftharpoons Al(OH)_3 + H^+ \tag{3}$$

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ \tag{4}$$
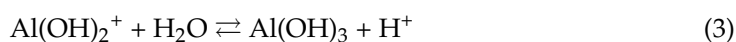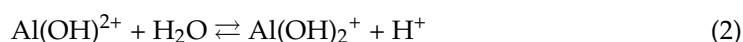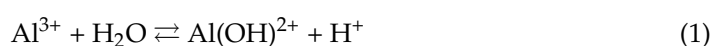
These chemical reactions demonstrate that one mole of Al^{3+} hydrolysis results in the production of three moles of H^+. The predominant Al species in acid soils are the mononuclear species ($AlOH^{2+}$, $Al(OH)_2{}^+$, $Al(OH)_3$, and $Al(OH)_4{}^-$) (Figure 1). Larger polynuclear hydroxyl Al species also form as metastable intermediates during $Al(OH)_3$ precipitation. The mononuclear Al^{3+} species appears to be most toxic at low pH, where it exists as an octahedral hexahydrate [37]. Aluminium phytotoxicity results in rapid inhibition of root growth because of the impedance of cell division and elongation, thus reducing water and nutrient uptake, which induces poor plant growth [38,39]. Tsado et al. [40] stated that, as soils become increasingly acidic, an essential nutrient such as P becomes less accessible to plants because of adsorption or precipitation, and more than 80% of P becomes immobile and inaccessible for plant uptake.
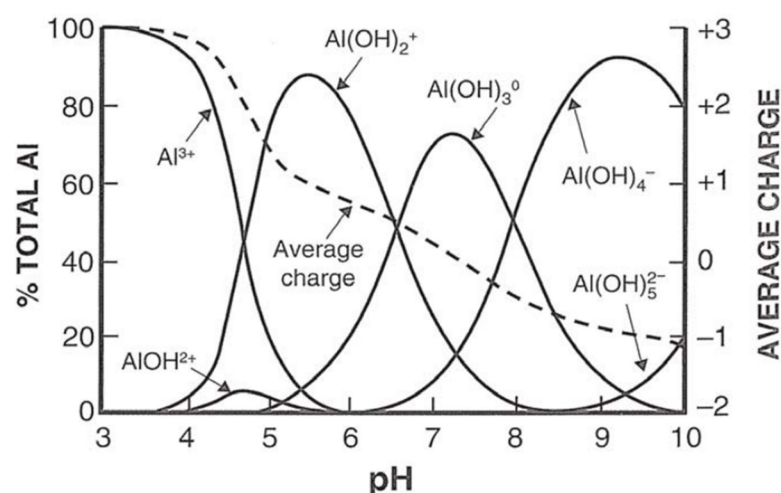
Figure 1. Relationship between pH and the distribution of soluble aluminium species [41].

3. Phosphorus

Phosphorus is important for plant growth and productivity. The concentration of P accounts for approximately 0.05 to 0.5% of the total plant dry weight [42]. Although the amount of P in soils is 2000-fold higher than that in plants, fixation by Al and Fe, or Ca and Mg, makes most P unavailable to plants. Thus, plants experience P deficiency in most agricultural fields. In the early stages of plant development, it is difficult to diagnose P deficiency because the only symptom usually observed is stunting, which is a very general symptom. In plants, P is highly mobile and can be translocated from older to younger plant tissues and actively dividing tissues when deficient [43]. Most P is translocated to the fruiting areas of the plant because high energy is required for seeds and fruit production. Diagnosis error may occur while determining P deficiency because the appearance of a purplish colour on the veins of young leaves may also be a symptom of N deficiency [44]. The difference is that a P-deficient plant will not have any chlorosis. Moreover, P deficiency slows development; therefore, the plant will take a longer period to mature, in addition to having a lower quality and quantity of the crop yield [45]. Malhotra et al. [42] claimed that a lack of P reduces crop yields on 30 to 40% of the world's arable land. To solve this problem, a large amount of phosphate fertiliser is needed to correct the P deficiency. However, the P use efficiency (PUE) is only within the range of 15 to 20% in agricultural fields. Hence, most of the soil-applied P is leached out before plant uptake and this may result in surface water eutrophication [46].

3.1. Significance of Phosphorus in Plants

Phosphorus plays a significant role in several cellular processes, including maintenance of membrane structures, production of biomolecules, and synthesis of energy [47]. Moreover, P aids in cell division and enlargement [48], regulation of enzymatic activity, and carbohydrate metabolism [49]. Plant development processes, such as seed germination, root and shoot development, stalk and stem strengthening, and flower and seed formation, in addition to yield quantity and quality, are interrelated with P [50,51]. Additionally, the N-fixing capacity of leguminous plants increases with increasing P availability. Furthermore, P is a vital constituent of cellular energy transfer because it is part of adenosine triphosphate (ATP), cytidine triphosphate (CTP), guanosine triphosphate (GTP), uridine triphosphate (UTP), phosphoenolpyruvate, and other phosphorylated intermediate compounds [42]. It is also an essential component of nucleic acids, such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Thus, its presence is important in reproduction and protein synthesis. Plants undergo several morphological, physiological, and biochemical adaptations to sustain their functions under inorganic phosphate (P_i-deprived conditions). These adaptations include root architecture, organic acid exudation, and alternative glycolytic and respiratory pathways [52].

3.2. Dynamics of Phosphorus in Soil–Plant Systems

The main origin of P in the biosphere is the weathering of primary minerals, such as apatite and P additions in the form of commercial fertilisers, plant residues, and agricultural wastes [53]. Weathering of geologic materials, such as igneous, sedimentary, and metamorphic rocks, is the primary source of P in agricultural systems. However, the amount of P released is not significant for an optimum crop production. Phosphorus is released into soils for plant uptake through chemical processes (precipitation and dissolution of primary and secondary minerals), physico-chemical processes (adsorption and desorption of P from clays, oxides, and minerals) and biological processes (immobilisation and mineralisation of P in organic materials into inorganic forms) [54–56].

Phosphorus is used as an orthophosphate in a completely oxidised and hydrated form. Plants absorb P either as ions of the primary monobasic phosphate, $H_2PO_4^-$, or those of the secondary dibasic phosphate, HPO_4^{2-}, depending on the soil pH [57,58]. A portion of absorbed inorganic P is rapidly transformed into organic molecules after entering plant roots or after being transported to the shoot. The P used by plants is returned to soil as organic phosphates in either plant or animal residues. Thereafter, these residues undergo mineralisation to produce inorganic phosphate for plant uptake. In addition to mineralising organic P, some microorganisms such as *Aspergillus, Arthrobacter, Pseudomonas*, and *Achromobacter* also secrete organic acids, such as α-ketogluconic acid, which attaches insoluble Ca phosphates and later releases the phosphate. The rates of mineralisation and immobilisation are attributed to the C:P ratio of residues in the soil. Menzies and Lucia [59] divided the C:P ratio into three categories based on the probability of organic P being mineralised or immobilised once returned to the soil: when the C:P ratio is less than 200:1, net mineralisation prevails; when the C:P ratio is between 200:1 and 300:1, immobilisation and mineralisation rates are relatively equal; and when the C:P ratio is greater than 300:1, net immobilisation occurs.

3.3. Phosphorus Forms in Soils

Soil P is commonly present in either inorganic (P_i) or organic (P_o) forms [47] and the proportions of P_i and P_o change as soils develop. Inorganic P fractions comprise soluble and loosely bound P, Al-P, Fe-P, Ca-P, reductant soluble P, and occluded P, whereas organic P fractions include inositol P, nucleic acid, and phospholipids [50]. The two P forms behave differently because they undergo different reactions in soils [60,61].

Approximately 50 to 75% of the soil's total P comprises P_i and, in some cases, it may range from 10 to 90% [62]. Inorganic P is generated when primary minerals are weathered or through the application of inorganic P fertiliser and organic amendments. The release of available P through mineral weathering occurs slowly because the primary P minerals (apatite, strengite, and variscite) are very stable, and thus cannot satisfy crop requirements. In contrast, the dissolution rate of secondary P minerals (Ca, Fe, and Al phosphates) depends on the mineral's size and the soil pH [63,64]. With increasing soil pH, Fe and Al phosphates solubilises easier; however, Ca phosphates are harder to dissolve, with the exception of pH values higher than 8 [65]. The desorption reaction enables adsorbed P to be released into the soil solution from the surfaces of clays and Fe or Al oxides. These P forms exist in complex equilibrium with each other, representing the range from very stable, sparingly available P to plant-available P pools, such as labile P and solution P [56].

Organic P is composed of 30 to 50% of the total P in soils [66,67]. It is derived from soil organic matter, crop residues, and various manures following decomposition and mineralisation by soil microorganisms. Soil P_o predominantly exists in stable forms such as inositol phosphates and phosphonates, and active forms such as orthophosphate diesters, labile orthophosphate monoesters, and organic polyphosphates [68,69]. Organic P is released through the mineralisation processes induced by soil organisms and plant roots associated with phosphatase secretion [56]. According to Wang et al. [70] and Turner et al. [68], phytate (inositol hexa- and penta-phosphates) is the most abundant inositol phosphate in the soil. It constitutes approximately 60% of soil P_o [71]. Fifty-one million tons of phytate is found

each year in commercially produced fruits and crop seeds [72]. Phytate is the principal storage form of P in seeds of cereals and grains, and it is hydrolysed (dephosphorylated) during germination by intracellular plant phytases [73,74]. Dephosphorylation of phytate is important to supply P_i to young seedlings [75,76]. However, if the seeds do not germinate, their phytate fills the pool of soil phytate. Mineralisation entirely depends on soil moisture, temperature, surface physical chemical properties, and soil pH and Eh (for redox potential) [56]. Generally, the bioavailability of P in soils is reliant on the transformation of P_o [61]. Therefore, a systemic evaluation is required to understand that the complexity of soil P availability is closely linked to P dynamics and transformation among different P pools.

3.4. Phosphorus Pools

The total P in soils usually ranges from 50 to 3000 mg kg^{-1}, depending on the parent materials, soil types, and soil management practices [54]. However, only a small proportion of the total P is available for plant uptake because most P in mineral soils is associated with Al and Fe oxide or hydroxide in acidic soils, and with Ca in calcareous soils [77,78]. Phosphorus in the soil solution ranges from <0.01 to 1 ppm [47]. The bulk of the soil P exists as groups of compounds, namely, organic P, Al-bound inorganic P (Al-P_i), Fe-bound inorganic P (Fe-P_i), and Ca-bound inorganic P (Ca-P_i) [79]. Most of the P in each group has very low solubility and is not readily available for plant uptake; however, all of these forms slowly contribute P to the soil solution [2,65].

There are three pools of P in the soil–solution–plant system, namely, soil solution P, labile P (active P), and non-labile P (fixed P). Phosphorus in the forms of orthophosphate ions ($H_2PO_4^-$, HPO_4^{2-}) is named soil solution P because it is present in the soil solution. The monovalent anion ($H_2PO_4^-$) dominates in strongly acidic soils (pH 4 to 5.5) and divalent anions (HPO_4^{2-}) predominate at higher pH conditions. This P pool is usually readily available for plant uptake or to be transformed into secondary minerals. Labile P (Al-P, Fe-P, and Ca-P) is the fraction of P that is taken up by the crop and is chemically mobile, exchangeable, and reactive in soil and water. The labile or more bio-available phosphate is adsorbed onto the surfaces of more crystalline compounds, such as sesquioxides or carbonates. This P is held to soil particles and organic matter by relatively weak bonds. Labile P pool replenishes the dissolved P every time the concentration of P in soil solution decreases [80]. The non-labile part (occluded P, reductant soluble P, and residual P) corresponds to a fraction of P that is not readily available for plants because of complexation with metal oxides and hydroxides or is bound within mineral compounds such as apatite [81]. The non-labile P is hard to solubilise; thus, the conversion of non-labile to labile and soil solution P is slow [82]. Non-labile P is only available through the dissolution of primary and secondary minerals. The P in these three pools exists in an equilibrium, in which they are continuously converted from one pool to another. For example, when plants take up P from the solution, it is replenished by the labile fraction, which in turn is more gradually replenished by the non-labile fraction.

4. Phosphorus Retention and Release Mechanisms in Soils

The ambiguity and difficulty in managing P requirements for plants in most agricultural systems has long been recognised. Because soils are not only highly deficient in P, the availability of P from applied sources tends to decrease. Several chemical reactions have been reported to regulate the retention or release of P in soil systems causing P transformation. Alteration of soil pH controls P retention in soils by adsorption and precipitation reactions of P with Fe and Al oxides, clay minerals, and calcium carbonate ($CaCO_3$). Conversely, the mechanisms by which P is released into the soil solution are the dissolution of primary and secondary minerals; desorption of P from clays, oxides, and minerals; and mineralisation and solubilisation processes mediated by phosphate solubilising microorganisms (PSMs).

4.1. Precipitation and Adsorption Reactions

Both precipitation and adsorption reactions are involved in the retention mechanism of phosphates. When the orthophosphate concentration is low, the dominant process is the adsorption of phosphate ions onto the surfaces of more crystalline clay compounds, sesquioxide's, or carbonates [66,83,84]. On the contrary, when the orthophosphate concentration is high, soluble P precipitates with metal cations to form Fe and Al phosphates in acidic soils, and Ca and Mg phosphates in alkaline soils [45,66,84]. It is believed that the adsorption process is essential in managing the availability of P over a shorter time frame [45].

When soluble P is applied to soils in the forms of fertilisers or amendments, a rapid increment of soil solution P concentration is noted. Afterwards, these P portions undergo precipitation or adsorption processes to decrease their solubility [85]. These chemical reactions are pH dependent. In acidic soils, Al and Fe ions usually form precipitates with approximately all the dissolved $H_2PO_4^-$ ions (Figure 2). These precipitated hydroxyl phosphates are insoluble; thus, their P content becomes almost unavailable to plants.
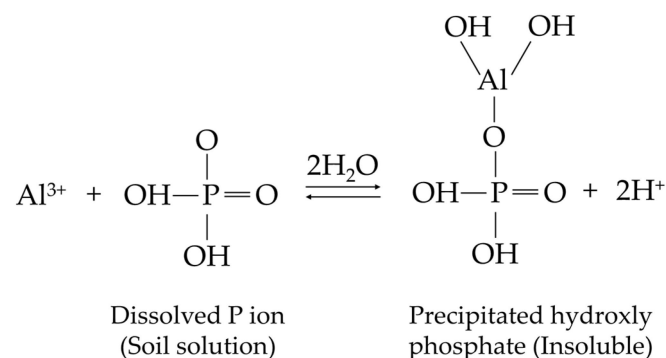
Figure 2. Precipitation reaction in the phosphorus fixation process [47].

The anion exchange reaction occurs when negatively charged orthophosphate ions are attracted to positive charges that develop under acidic conditions on the surfaces of Al or Fe oxides and the broken edges of kaolinite clays [79,86] (Figure 3). Outer-sphere complexes are formed through this process. These complexes are formed using weak reversible electrostatic bond because the bonding consists of a water molecule located between the anion and surface [7].
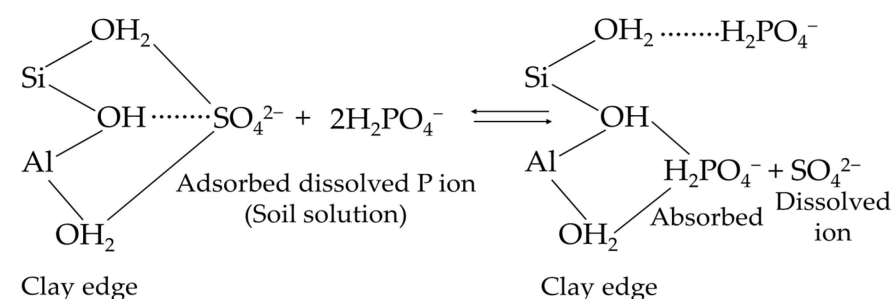
Figure 3. Anion exchange reaction in the phosphorus fixation process [47].

The formation of the inner-sphere complex occurs when orthophosphate ions replace the hydroxyl groups on the surface of Al or Fe oxides and hydroxides, or the clay surface. This process is recognised as specific adsorption or the ligand exchange reaction [39,87,88]. In this reaction, a strong covalent bond is formed between the phosphate and a valence unsatisfied surface with no water molecule occurring between the sorbent and sorbate [7]. For example, in the first step in Figure 4, P is bound to one Al ion through an Al-O-P bond, and at this stage P is still labile. In the second step, the second oxygen of the P replaces a second hydroxyl, forming a ring structure with two Al ions. After this reaction, the

possibility of P being desorbed into the soil solution is extremely low because it becomes an integral part of the oxide mineral [47,89].
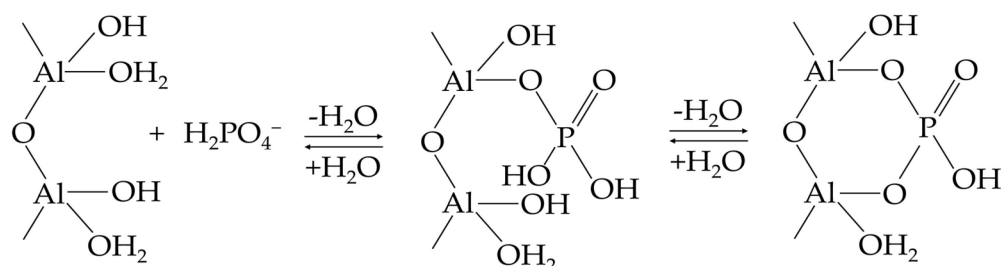
Figure 4. Phosphorus adsorption via ligand exchange on aluminium oxides [47].

With further reactions, adsorbed P is trapped on the surface of soil minerals if any Fe or Al oxide coating is precipitated on the mineral. The trapped P is then described as occluded P (Figure 5). Thus, the ligand exchange reaction and surface precipitation are considered to exist on a continuum that sometimes occurs simultaneously because precipitation can occur rapidly if solution P concentrations are highly elevated [7].
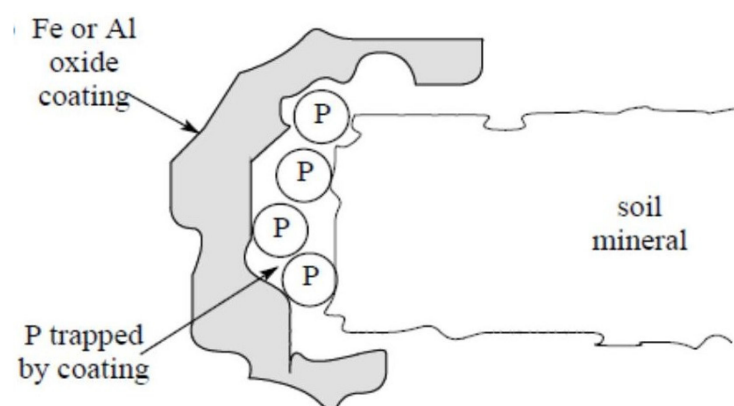
Figure 5. The occlusion of adsorbed phosphorus [90].

In neutral-to-calcareous soils, P retention is dominated by precipitation reactions [91] with Ca to form a sequence of products decreasing solubility [86], although P can also be adsorbed on the surface of $CaCO_3$ [92] and clay minerals [93]. For example, monocalcium phosphate added to soils rapidly reacts with $CaCO_3$ to form dicalcium phosphate, and further reaction transforms dicalcium phosphate into octocalcium phosphate or hydroxyapatite, which are more stable phosphate forms [94]. The solubility of these phosphates increases with decreasing soil pH [95]. Therefore, P is most accessible in the pH range of 6.5 to 7.0 [96,97]. Any deviation from this pH range alters the charge of P species in soil solution and on the surface of the adsorbing particles.

4.2. Dissolution, Desorption, and Mineralisation Reactions

Dissolution is the process in which phosphate minerals dissolve to release P. Hydrogen ions are essential for the dissolution of soil minerals and they usually originate within the soil itself or exudate from roots or microbes and sinks for Ca and P [54]. Applications of organic materials to soils increases P availability by unlocking P fixation. Organic amendments increase P availability directly and indirectly: directly by adding P to the soil and indirectly by releasing organic acids, which block P adsorption sites in the soil, and change the soil pH and the complexation of soluble Al and Fe [98].

Desorption is the inverse response of sorption and defines the detachment of sorbed P from clays, oxides, and minerals into soil solution through diffusion along the concentration gradient [63,99]. This occurs when removal of P from the soil solution by plant uptake

reduces the soluble P levels to a small amount and induces a concentration gradient that facilitates the slow release of adsorbed P from soil constituents as a response to maintain solution equilibrium (replenish the soil solution P). This feedback mechanism is usually not rapid enough to ensure sufficient P availability in highly cultivated areas, especially when there is lack of added P through fertilisation, manuring, or crop residue application [99].

In addition to dissolution and desorption reactions, mineralisation and microbial P-solubilisation can release and increase the available P. In the natural environment, numerous microorganisms in the soil and rhizosphere are effective at releasing P from total soil P via mineralisation and solubilisation [100]. Microbes that transform insoluble P_i and P_o to soluble P forms and regulate biogeochemical P cycling in soil system are known as phosphate solubilising microorganisms (PSMs) [101]. Phosphate solubilising microorganisms are classified as phosphate solubilising bacteria (PSB), which include *Bacillus* sp., *Pseudomonas* sp., and *Rhizobium* sp.; phosphate solubilising fungi (PSF), which include *Penicillium* sp., *Aspergillus* sp., and *Rhizopus* sp.; phosphate solubilising actinomycetes (PSA), such as *Streptomyces* and *Micromonospora*; and cyanobacteria [102,103]. These microorganisms serve as mediators in the soil P cycle to mineralise organic P and solubilise inorganic P minerals and store large amounts of P in biomass [104,105]. They transform insoluble P_i to soluble orthophosphate forms by secreting different organic or inorganic acids that release H^+ and lower the medium pH [103,106]. Moderately labile Pi, such as Al-P and Fe-P, can be made available to soil organisms through organic acid excretion by PSMs, which in turn chelate Al and Fe ions, allowing P to be liberated [107]. The carboxyl groups of organic acids can bind P by replacing cations or compete for P adsorption sites, enhancing the soil absorption of PO_4^{3-} and increasing P_i solubilisation [101].

5. Factors Affecting Phosphorus Availability in Soils

Mineral dissolution, desorption of adsorbed P from soil constituents, and organic matter mineralisation are the processes that replenish phosphate into the soil solution [63]. The accessibility of P to plants depends on the soil characteristics that determine the degree of sorption and desorption of P. These include clay content and mineralogy, organic matter, soil pH, and exchangeable Al, Fe, and Ca concentration in the soil solution [83,108,109].

5.1. Clay Content and Mineralogy

Phosphorus release is controlled by Fe and Al content and the percentage of clay in acidic soils [110]. Havlin et al. [86] stated that P is adsorbed most extensively by Al and Fe oxides and, to a greater extent, by 1:1 clays (such as kaolinite) compared with 2:1 clays (such as montmorillonite) because of the presence of higher Fe or Al oxide contents in the former clay minerals. In other words, the greater the surface area exposed with a given type of clay, the greater the tendency to adsorb P [111]. Phosphate is strongly adsorbed on the surfaces of clay by replacement of hydroxide ion (OH^-) from clays. Moreover, the amount of clay present in a soil profile has a profound influence on the degree of P retention, with P retention being higher in soils with high clay content compared with sandy textured soils [63,96].
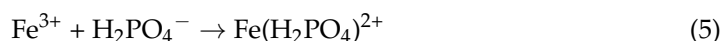
5.2. Organic Matter

Addition of organic matter can improve P availability through solubilisation of fixed P by soil microorganisms, in addition to complexation (chelation) of soluble Al and Fe by organic molecules [97,112,113]. Organic matter is made up of humic substances that have many negative charges and functional groups, such as carboxyl, hydroxyl, and carbonyl. These functional groups react with Al and Fe to form stable complexes, thus preventing their reaction with P [114,115]. Nader et al. [116] and Paulo et al. [117] reported that organic material can form a protective cover by coating sesquioxides to reduce P adsorption; thus, more P is released for plant uptake. Moreover, mineralisation of organic matter produces low molecular weight organic acids, such as citric, oxalic, tartaric, and malic acids. This reaction reduces the adsorption of P on soil colloids by strongly competing for

the adsorption sites [56,118]. Furthermore, these organic acids have the ability to dissolve Ca phosphate. For example, citric acid can efficiently weaken the nanoparticle stability of hydroxyapatite (HAP) by regulating free Ca availability [119]. In addition, Gerke [74] opined that the excretion of citrate and oxalate by plant roots is a promising means of improving inositol hexakisphosphate (phytate) solubility in soil and its P acquisition by the roots. This is because, in high P fixing soils, the excretion of di- and tricarboxylic acid anions, mainly by citrate and oxalate, can enhance the mobilisation of P_i anions [120]. These di- and tribasic anions can desorb the P_i anion from the soil solid phase via ligand exchange, in which the P_i at the soil solid is replaced with the carboxylate anion. Moreover, organic anions have the ability to dissolve Fe and Al, thereby destroying the P_i sorption sites [74]. In addition, the carboxylate anion can dissolve humic molecules to which the P_i anion is bound through Fe or Al bonds, resulting in the release of P_i as a humic–Fe(Al)–P complex [121].
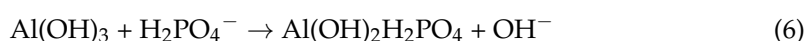
5.3. Soil pH, Exchangeable Aluminium, Iron and Calcium Concentration

Soil pH plays an important role in the bioavailability of orthophosphates. Soil pH can affect the presence of metal cations, which precipitate with orthophosphate, and the ability of Fe and Al oxides to hold P ions [65,66]. A pH range of 6.5 to 7.0 is the optimal pH in terms of P availability in soils [7]. Highly exchangeable Al and Fe ions are a problem in acid soils because orthophosphate can be locked from the soil solution [122–124]. Orthophosphates in soil solution form amorphous Fe-P and Al-P compounds, which are water-insoluble through reactions with Fe and Al species [97,125]. In acidic soils, there are two mechanisms of which P is made unavailable, specifically, via precipitation of P by Al, or Fe and sorption by oxides and hydroxides of Al or Fe (gibbsite, haematite, and goethite) [126,127]. The following equations provide further explanation.
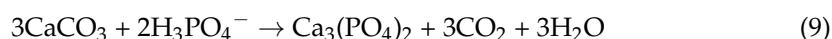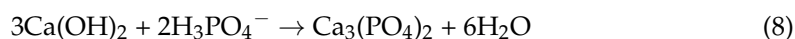
Precipitation of P by Al or Fe:

$$Fe^{3+} + H_2PO_4{}^- \rightarrow Fe(H_2PO_4)^{2+} \tag{5}$$

Sorption by hydroxide of Al and Fe:

$$Al(OH)_3 + H_2PO_4{}^- \rightarrow Al(OH)_2H_2PO_4 + OH^- \tag{6}$$

$$Fe(OH)_3 + H_2PO_4{}^- \rightarrow Fe(OH)_2H_2PO_4 + OH^- \tag{7}$$

In alkaline and calcareous soils, soluble P reacts with Ca ions and $CaCO_3$, forming low-solubility calcium phosphates [128]. This reaction decreases P availability. This is represented by the following equations:

$$3Ca(OH)_2 + 2H_3PO_4{}^- \rightarrow Ca_3(PO_4)_2 + 6H_2O \tag{8}$$

$$3CaCO_3 + 2H_3PO_4{}^- \rightarrow Ca_3(PO_4)_2 + 3CO_2 + 3H_2O \tag{9}$$

Sodium phosphates are formed in strongly alkaline soils because of the high amount of Na. However, P availability is not an issue in soils with pH values above 9 because sodium phosphates are soluble. However, other factors cause the inhibition of the plant growth in such adverse conditions [96]. For example, concentrations of micronutrients (Cu, Fe, and Zn) in the soil become lower when P availability increases at high pH [80,129].

6. Potential of Using Organic Amendments to Mitigate Productivity of Phosphorus Fixing Soils

Organic amendments were initially seen only as a source of nutrients, especially nitrogen (N) [130]. To date, other contributions of organic amendments have been highlighted in research. These include improvement of soil moisture status, increase in soil pH and organic matter content, promotion of the release of soluble humic materials and soluble aliphatic organic acids, and reduction of P sorption capacity [131] (Figure 6). Studies have shown that organic amendments can directly increase the P pool in soils and affect the

adsorption and desorption of P in soil [132,133]. However, organic and mineral inputs cannot be fully substituted, but both are equally important for sustainable crop production [134,135]. One key complementarity is that organic resources improve the status and the functions of soil organic matter, whereas mineral inputs are aimed at key nutrient limitation [131].
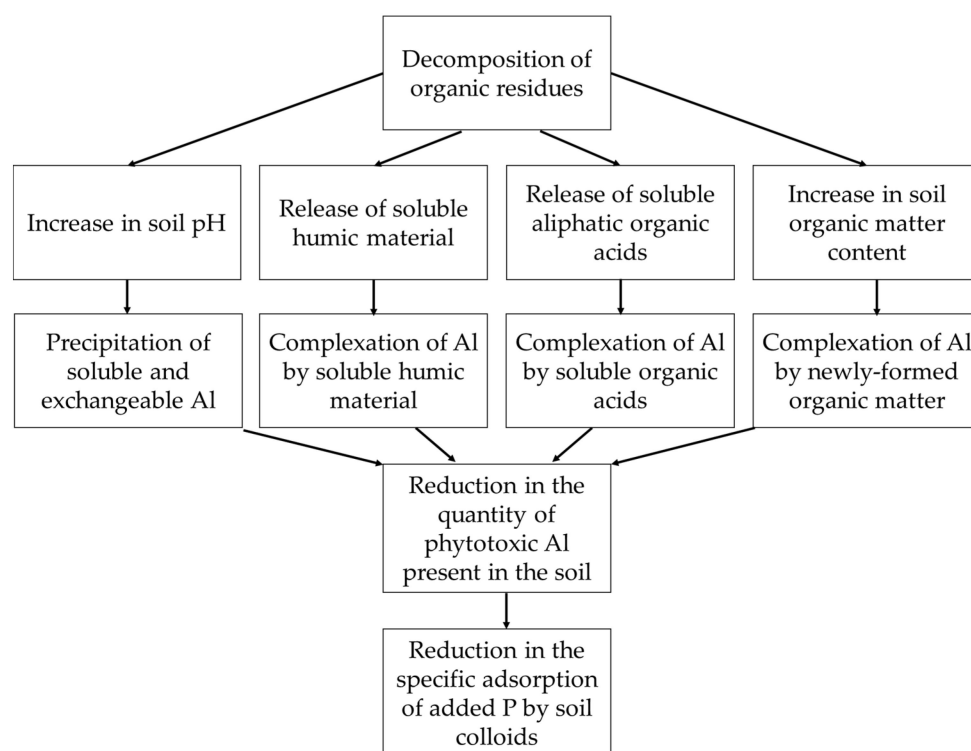

Figure 6. A conceptual model of major processes that lead to a reduction in the phytotoxic aluminium present in the soil and the increased phosphorus availability when organic amendments are added to the soil [131].

The proposed mechanisms that may explain the initial rise in soil pH when organic amendments are applied to soils are as follows: (i) oxidation of organic acid anions present in the decomposing residues; (ii) ammonification of organic N in the applied residue; (iii) specific adsorption of organic molecules produced during residue decomposition; and (iv) reduction reactions induced by anaerobiosis [123,131]. Plant material and animal wastes generally have excess cations over inorganic anions and the balance is maintained by synthesis of organic acid anions, such as oxalate, citrate and malate [123]. Oxidation of these organic acid anions during decomposition of plant material and animal wastes is likely to contribute to an increase in pH. Yan et al. [136] demonstrated that the increase in soil pH following the addition of malate and citrate is correlated with CO_2 evolution during the decomposition of these two anions. The added organic acid anions are able to complex protons (H^+), and these account for any immediate rise in soil pH.

6.1. Compost

Amending acid soils with compost or a mixture of compost and biochar can increase total P, available P, inorganic P fractions (soluble-P, Al-P, Fe-P, redundant soluble P, and Ca-P), and organic P [13]. Similar findings were reported in the work of Sanusi et al. [137] and Ch'ng et al. [8], where rice straw compost with Christmas Island rock phosphate (CIRP) was found to increase soil-available P in acidic soil. Another study by Mensah and Frimpong [138] showed that the application of compost significantly increased the soil-available P in both the Aiyinase and Cape Coast soils. This was possible because compost increased soil pH and exchangeable bases, while reducing exchangeable acidity,

exchangeable Al, and exchangeable Fe. In addition, the incorporation of compost in highly weathered soils can enhance the dissolution and immobilisation of phosphate rock [139,140]. Furthermore, the addition of compost to soils can prevent soil P sorption because P sorption sites and the bonding energy for phosphate sorption to the soil solid phase decreases, resulting in an increase in soil P availability [141].

6.2. Animal Manure

Gichangi et al. [142] revealed that addition of goat manure decreased sodium hydroxide-extractable inorganic P ($NaOH$ P_i), but increased sodium bicarbonate ($NaHCO_3$) and resin P fractions, indicating that goat manure decreases fixation of added P. Furthermore, manure contains significant amounts of P_o, such as phospholipids and nucleic acids, which are released to increase soil P_i concentrations by mineralisation [143]. Parham et al. [144] found that long-term application of cattle manure increased C of microbial biomass and dehydrogenase activities and enhanced activities of enzymes involved in the transformation of P. Moreover, higher pH and lower oxalate extractable Al were recorded following the introduction of cattle manure to the soil and the effect continued throughout the eight-week incubation period [145].

6.3. Biochar

A meta-analysis by Glaser and Lehr [146] demonstrated that biochar has the potential to enhance plant-available P and could be a sustainable strategy to complement conventional P fertilisers. Chintala et al. [147] reported that incorporation of biochar into acidic soils at 40 g kg^{-1} increased equilibrium solution P concentration and available sorbed P. Application of coffee husk biochar to acidic soils improved pH from 5.08 to 6.66, resulting in a large enhancement of available P content from 4.52 to 23.4 mg kg^{-1} [148]. In acid soils, small increases in pH can lead to substantial reductions of P interactions with soil minerals because of the formation of mineral–organic matter complexes, which have a lower P sorption capacity compared with Al and Fe oxides or hydroxides [149,150]. Liu et al. [151] reported that application of 40 t ha^{-1} of rice hull biochar to red clay soil and alkaline soil increased the availability of P by 52.63 and 33.37%, respectively. Similarly, amending poultry litter-based biochar at a rate of 10 t ha^{-1} increased the bioavailable P in the soil by >1000-fold [152]. Additionally, it has been reported that biochar application facilitates the growth of mycorrhizal fungi and the survival rate of soil P solubilising bacteria, which in turn affects the solubility of endogenous P in soils [153]. Trippe et al. [154] found that P levels were higher in mine tailings amended with lime, biochar, biosolids-locally-sourced microbial inoculum (LBB-LSM) compared with the control treatment, which was lime only. Moreover, in the post-harvest nutrient content analysis, tailings treated with lime only had significantly less available P than the LBB-LSM treatment. Page-Dumroese et al. [155] observed similar increases in K, P, Ca, and Mg in a field experiment in which biochar and biosolids were used to amend mine tailings.

6.4. Crop Residues

The decomposition of crop residue serves as an important source of P to crops and other organisms [156]. A high proportion of P in crop residues exists as orthophosphate and has the potential to be returned to the soil in a readily available form, which would be available to assimilation by crops (via root uptake) and microorganisms, in addition to sorption onto soil minerals [156]. For P in particular, the application of crop residues positively improves soil P availability because it enhances phosphatase enzyme activities [157]. Crop residues can enhance labile P, exchangeable P, and mineralisable organic P, and Ca-bound P fractions, but they decrease P fractions that are associated with Al and Fe oxide minerals [158].

7. Charcoal and Its Properties

Charcoal is the main solid product generated from carbonisation of biomass, a slow pyrolysis (maximum of 10 °C min^{-1}) that occurs under limited oxygen or no oxygen conditions [159]. Charcoal is mainly used as a smoke-free fuel for cooking, heating, and steel production. Approximately 20 million tonnes of charcoal were produced worldwide in 2015, which was three times higher than in 1961 [160]. The chemical and physical properties of charcoal depend on the species of timber used, the soil in which the tree grows, and the process of pyrolysis, whether fast or slow, and the highest temperature attained (volatile matter) [161]. In addition, charcoal is an amorphous carbon in the form of highly porous microcrystalline graphite [162]. It is predominantly made up of irregularly arranged aromatic rings and has a high initial carbon density (70 to 85%) compared with typical woody biomass (<50%) [163,164]. These aromatic structures are stable and are responsible for the recalcitrance of charcoal [165].

The fresh charcoal from an opened kiln has a low moisture content, which is usually less than 1% but it can rapidly absorb approximately 5 to 10% of the moisture content from the humidity of the air itself over time [166]. The volatile matter in charcoal ranges from 40% to less than 5% [167]. Generally, charcoal produced at a low temperature has higher value of volatile matter than charcoal produced at a high temperature. In addition, the high-volatility charcoal tends to be stronger, heavier, harder, and easier to ignite than low-volatility charcoal. The high-volatility charcoal also burns with a smoky flame compared with the low-volatility charcoal. Therefore, the former type of charcoal is preferable for domestic use, such as barbecues, cooking, and heating, whereas the latter type is preferable for other utilisations, such as metal manufacture and chemical purification.

Effects of Charcoal in Agriculture

Charcoal affects both physical and chemical properties of the soil quality. The application of charcoal improves soil water retention and aggregation. Charcoal is known to have a high surface area because of its porous nature. As a result, soil water retention increased by 18% upon addition of 45% charcoal to a sandy soil [168]. Previous studies have shown that soil water-holding capacity increases with the introduction of agricultural residues, such as green manure, organic wastes, and coal-derived humic substances [169,170]. The potential mechanisms by which coal-derived humic acids improve soil physical properties are the formation of organo-mineral complexes by functional groups of the humic acids [171]. The hydrophobic polyaromatic backbone limits the flow of water into the aggregate pores, thus increasing aggregate stability and water availability.

Moreover, charcoal increases pH and decreases Al saturation of acid soils, especially in highly weathered soils of the humid tropics [172]. Application of charcoal with a significant amount of ash releases free bases such as K, Ca, and Mg into soils for plant use [173]. In addition to the nutrient contents, the nutrient retention can also be improved through application of charcoal [174,175]. Additionally, studies showed that crop yields can be enhanced if charcoal is co-applied with inorganic or organic fertilisers compared with control soils [173,176]. Moreover, charcoal removes pollutants such as Pb, As, and Hg from soils and water. The detoxifying capability of charcoal is directly related to the increase in specific surface area that occurs during pyrolysis [177,178]. Furthermore, because of its relative inertness, the use of charcoal as a soil conditioner is currently recognised as a mitigation strategy for soil-based greenhouse gas (GHGs) emissions by directly sequestering solid C in the ground for hundreds or even thousands of years [179]. This is because charcoal is considerably more recalcitrant than soil organic matter and decomposes very slowly.

8. Wood Ash and Its Properties

Wood ash is an inorganic residue produced from the combustion of wood and wood products, such as chips, saw dust, and bark [180]. Physical and chemical properties of ash differ depending on the plant species, plant sources, plant parts used for

combustion, process parameters during incineration, and storage conditions of combustion residues [20,181]. Moreover, the leaching properties of ash are influenced by post-combustion treatments, such as self-hardening, thermal treatment, or hardening with the addition of a binding agent (potassium silicate) [182]. Hardwoods usually produce more ash than softwoods, and the bark and leaves typically have 5- to 10-fold higher levels of ash than those of stem wood [183–185]. On average, the burning of wood results in approximately 6 to 10% ashes. When the combustion temperature was raised from approximately 550 to 1100 °C, the yield of wood ash decreased by 45% [186].

The average particle size of the wood ash is estimated to be 230 μm [186]. Naik [187] revealed that wood ash, as a heterogeneous mixture of particles of different sizes, is generally angular. Moreover, ash contains all of the components of wood in a concentrated form, with the exceptions of C, H, and N, which vaporise during combustion. However, because of incomplete combustion of biomass, a small amount of remaining C can be found in the ash, usually as charcoal [188]. The major elements present in wood ash are Ca (7% to 33%), K (3% to 4%), Mg (1% to 2%), Mn (0.3% to 1.3%), P (0.3% to 1.4%), and Na (0.2% to 0.5%), whereas trace elements (Zn, B, Cu, and Mo) and others are in parts per million (ppm) [189]. The K in wood ash dissolves completely in water, which makes it likely to leach [20,190]. During application of wood ash in soils, it behaves like a fertiliser with a low N content (NPK: 1:10:50) [191].

Moreover, wood ash has liming effect because of the presence of certain neutralising compounds, such as calcite ($CaCO_3$), fairchildite ($K_2Ca(CO_3)_2$), lime (CaO), and magnesium oxide (MgO) [186,192,193]. The pH of wood ash generally ranges from 8.9 to 13.5 [20]. The neutralising capacity of wood ash is often expressed as $CaCO_3$ equivalents (CCE). Etiegni and Campbell [186] indicated that hydroxides of Ca, Mg, and K are the main contributors to the soluble alkalinity in wood ash. Upon application of wood ash, the change in pH is faster than that of lime because of the rapidly soluble content of oxides and hydroxides [25].

Effects of Wood Ash in Agriculture

The effects of wood ash as an inorganic amendment on the physical, chemical, and biological properties of soil are barely known. In terms of physical properties, wood ash addition to soils may have a significant impact on texture, aeration, water-holding capacity, and salinity. Wood ash is essentially composed of fine particles and its application may alter the texture of soils. Etiegni and Campbell [186] demonstrated that wood ash particles swell when mixed with water, making them capable of blocking soil pores. This increases water-holding capacity and enhances the supply of nutrients because nutrients are taken up in solution [181,194,195].

Although wood ash influences the physical properties of soil, the use of it as a soil amendment mainly modifies the chemical properties of soils. It can serve as a liming material and neutralising agent for acidic soil because of its high alkalinity [193,196,197]. This liming effect can be attributed to Ca and Mg carbonates in the ash, in addition to its fine structure [181]. As a result of the raised pH, wood ash can contribute to the reduction of Al toxicity and increase P availability [20,198]. Additionally, studies reported that exchangeable base cations, base saturation, and effective cation exchange capacity (ECEC) increased in ash-treated soil [199,200].

From a biological perspective, co-application of wood ash and an N source can potentially increase soil C and N microbial biomass, and the C mineralisation rate, thus leading to an increase in CO_2 production [196]. Furthermore, addition of wood ash to peat soils can also enhance the degradation of cellulose, resulting in an increased soil respiration rate [181]. A study by Hagerberg and Wallander [201] demonstrated that ectomycorrhizal mycelium populations are increased 2.4-fold due to the use of wood ash.
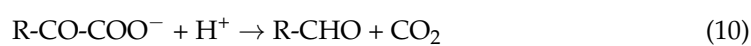
9. Mechanisms of Improving Phosphorus Availability Using Charcoal and Wood Ash as Organic and Inorganic Soil Amendments

Charcoal and wood ash are soil amendments that have the potential to improve P availability through several mechanisms. Both amendments contribute towards an increase in soil pH because of their alkaline nature. In addition, further decomposition of charcoal releases organic compounds, which eventually adsorb cations such as Al^{3+}, Fe^{2+}, and Ca^{2+}, which form complexes with P in the soil solution. Moreover, the highly porous structure of charcoal and wood ash can enhance P availability because they can hold nutrient-rich water through capillary action. Co-application of charcoal and wood ash can also increase P availability by directly releasing P from its particles.
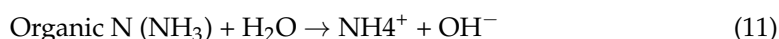
9.1. Amelioration of Soil Acidity upon Application of Charcoal and Wood Ash

Phosphorus fixation is weakest at a neutral pH and increases with increasing acidity. Similarly, metal cations such as Fe^{2+}, Al^{3+}, and Mn^{2+} are more available as pH declines into acidity, whereas, as pH increases into alkaline conditions, metal cations such as Ca^{2+} and Mg^{2+} become more available. A pH of 6.5 generally maximises P availability because there is minimal Al and Ca precipitation [84]. Addition of charcoal and wood ash to acid soils is believed to increase soil pH. The decarboxylation of organic acid anions and the ammonification of organic N are two mechanisms that cause soil pH to increase after application of charcoal [202,203]. During the oxidative decarboxylation of organic acid anions, proton (H^+) is consumed, carboxylate group is removed, and CO_2 is released, whereas the increase in soil pH during ammonification of organic N is attributed to the generation of OH^-.
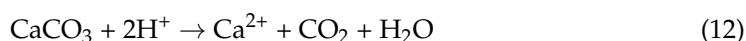
Decarboxylation of organic acid anions:

$$R\text{-}CO\text{-}COO^- + H^+ \rightarrow R\text{-}CHO + CO_2 \tag{10}$$

Ammonification of organic N:

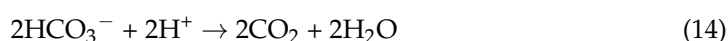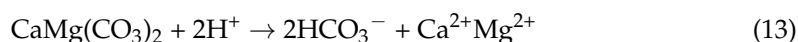$$\text{Organic N } (NH_3) + H_2O \rightarrow NH4^+ + OH^- \tag{11}$$

Moreover, charcoal and wood ash have high acid-neutralising capacity and can thus serve as liming agents. Liming agents contain Ca^{2+} or Mg^{2+} cations (sometimes both), and their supply has a neutralising effect, thus displacing the H^+ in the soil solution. A study by Risse and Harris [204] reported that the average $CaCO_3$ content of 37 industrial ash samples was 43%, with results ranging from 22 to 92%. The reaction of Ca^{2+} or Mg^{2+} with H^+ can form $CO_2 + H_2O$, which increases pH. The following equations illustrate the neutralisation processes of liming.

For limestone the reaction is:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \tag{12}$$

For dolomite the reaction is:

$$CaMg(CO_3)_2 + 2H^+ \rightarrow 2HCO_3^- + Ca^{2+}Mg^{2+} \tag{13}$$

$$2HCO_3^- + 2H^+ \rightarrow 2CO_2 + 2H_2O \tag{14}$$

For calcium silicate the reaction is:

$$CaH_2SiO_4 + 2H^+ \rightarrow Ca^{2+} + H_4SiO_4 \tag{15}$$

The concentration of Al^{3+} in solution decreases exponentially as soil pH increases. Therefore, co-application of charcoal and wood ash to acid soils has the potential not only to increase pH, but also to reduce Al toxicity. This reaction subsequently increases the availability of P in soils because the adsorption of P to Al and Fe oxides is reduced.

Aluminium or Fe phosphate solubility also increases with increasing soil pH, resulting in more free orthophosphates available for plant uptake.

9.2. Complexation of Aluminium and Iron by Humic Substances and Blockage of Phosphorus Adsorption Sites by Organic Acids

The slow decomposition of charcoal releases several organic compounds, namely, humic substances and organic acids. Humic substances contain various functional groups, such as carboxyl, alcoholic hydroxyl, and phenolic hydroxyl [205,206]. Negatively charged functional groups in humic substances can interact with positively charged minerals, such as Al or Fe oxides. This is because the functional groups have high affinity for Al and Fe. Therefore, the reaction of P with Al and Fe can be prevented and the availability of P in the soil can be improved. In addition, the low molecular weight organic acids produced during the breakdown of charcoal, such as citric, oxalic, tartaric, and malic acids, serve as anions that strongly compete with P for the adsorption sites on soil colloids. Organic acid anions are rapidly adsorbed on soil colloids compared with P, and this increases the concentration of P in the soil solution [207].

In fact, adsorption of organic functional groups onto Al or Fe can: (i) promote anion adsorption via cation bridges (Al^{3+} and Fe^{3+}); (ii) increase the specific surface area by inhibiting mineral crystal growth; (iii) alter surface charges; (iv) boost competition with other anions for adsorption sites; and (v) cause adsorbed anions to be desorbed [108,208–210]. Figure 7 demonstrates how P fixation by Al and Fe is mitigated upon application of charcoal.
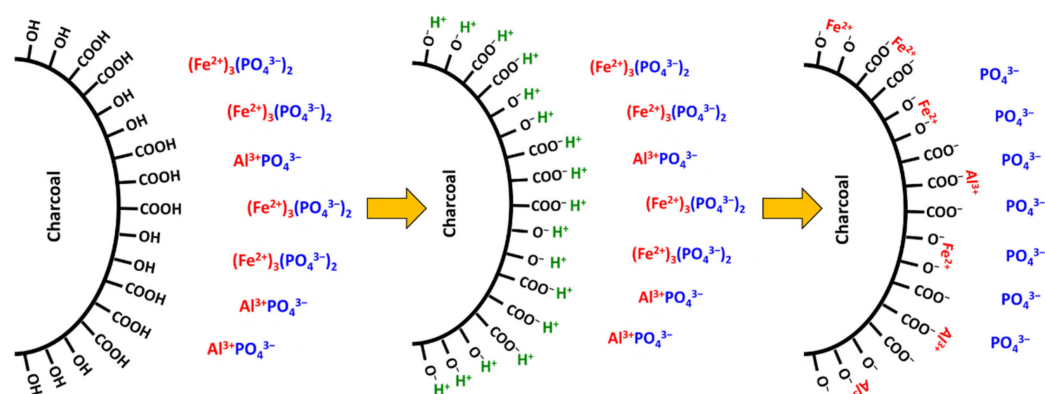

Figure 7. Proposed mechanism of the aluminium and iron chelation reaction at the negatively charged exchange sites of charcoal (adapted from Palanivell [211]).

9.3. Retention of Phosphorus-Rich Water by Porous Structure of Charcoal and Wood Ash

The addition of charcoal and wood ash to soils may have effects on the retention of water in the soil because of their sorption properties. The effect is related to the high internal porosity, high surface charge density, large surface area, and multiple functional groups, which aid the P adsorption [212,213]. Scanning electron microscopy (SEM) micrographs showed that the ash derived from pineapple residues also has porous structures [214]. The highly porous structure of charcoal and wood ash indirectly enhances P availability because they can capture and hold P-rich water, thus preventing them from leaching out. Charcoal can absorb organic and inorganic P in its pores, and lead to the formation of sparingly soluble phosphates that are subsequently released into the soil [213]. In addition, the hydrophilic property of wood ash causes it to expand when in contact with water. Hence, this increases the water-holding capacity and enhances the supply of P as P is taken up in solution. Furthermore, charcoal is reputed for its ability to adsorb P in the soil [150,215,216]. The electrostatic attraction by charcoal's positively charged sites makes it an efficient P adsorbent [217,218]. Shaaban et al. [219] reported that there is a positive correlation between the surface area of charcoal and the P sorption capacity, which can be explained by the pore-filling mechanism. Micropores within charcoal can strengthen the adsorption of mobile P, preventing it from leaching [173]. Moreover, charcoal has a

significant anion exchange capacity (AEC) because of the abundance of oxonium groups, hence enabling adsorption of insoluble P in the soil [147]. Additionally, Ca or Mg ions within charcoal can capture P via precipitation or cation bridges [147,218,220].

9.4. Direct Supply of Phosphorus from Charcoal and Wood Ash

Considering their chemical composition, charcoal and wood ash constitute good sources of major and minor elements and are therefore of interest in correcting certain nutrient deficiencies in soils [173,221]. Phosphorus may be present in charcoal as phytin, nucleic acid, and phospholipids. The slow decomposition of charcoal releases the P present in these compounds as orthophosphate ions. In addition, wood ash is essentially a direct source of major elements, such as Ca, Mg, K, and P, in soils. However, the effects of wood ash on P availability are strongly influenced by the composition of P in the wood ash itself. Pugliese et al. [222] and Omil et al. [223] reported that the concentration of extractable base cations and P increased in the soil amended with wood ash. A study by Gomez-Rey et al. [224] observed that, despite low P content in ash, soil-available P increased following wood ash application, which may be attributed to an increase in soil pH, resulting in the dissolution of soil P that was fixed as Al and Fe phosphates.

10. Conclusions

The availability of soil P is complex and needs to be systemically evaluated because it is highly associated with P dynamics and transformation among various P pools. It is essential to understand the chemical, physical, and biological processes or mechanisms governing P availability in soils, particularly the interactions of Al and Fe oxides with soil P, to ameliorate P fixation in acid soils. The integrated use of soil amendments, such as charcoal and wood ash, is believed to not only increase P availability, but also improve P use efficiency in acid soils. This is because negatively charged functional groups in organic substances of charcoal can interact with positively charged Al and Fe oxides, and thus alter P sorption in soils. The addition of wood ash to acid soils suggests that it may be used as a substitute for commercial lime because of its high acid-neutralising capacity, which is reputed to be capable of reducing soil acidity and the toxicity of Al and Fe. To address research gaps of using charcoal and wood ash on P transformation in soils, the aforementioned mechanisms need to be verified in laboratory and field experiments. Information on the optimum rates of charcoal and wood ash to improve P availability in acid soils can be obtained from these studies. In addition, in the presence of plants, the thresholds of charcoal and wood ash application rates to simultaneously ensure an adequate supply of nutrients and avoid toxicity can be revealed. Several planting cycles should be carried out to determine the beneficial residual effects of using these amendments.

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