Review

Phosphorus sorption in tropical soils

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Abstract: Phosphorus is an important primary nutrient required by plants in large quantities. The various forms of P that plants can take up are the primary monobasic phosphate ion ($H_2PO_4^-$), secondary dibasic phosphate ion (HPO_4^{2-}) and phosphate ion (PO_4^{3-}). In tropical soils, phosphorus adsorption is a major process that controls its availability to crops. Soils with low phosphorus adsorption capacity are often unable to supply adequate phosphorus to the growing crops thereby affecting their yields. This paper reviews the phosphorus adsorption phenomenon in a tropical soil. The review showed that Langmuir isotherm, Freundlich isotherm, Brunauer-Emmett-Teller (BET) isotherm, Dubinin-Radushkevich, and Temkin isotherm are the mostly used isotherms models for describing phosphorus adsorption. From the review, soil acidity and alkalinity, soil temperature and the electrical potential of clay surface are the main factors influencing phosphorus adsorption. Also, precipitation was discovered to be the main mechanism of P adsorption in tropical soils. Fertilization practices such as the addition of organic manure, crop residues, rock phosphate, water-soluble P fertilizers and incorporation of phosphorus solubilizing organism are highly recommended to increase P solubility and availability in highly weathered soil.

Keywords: adsorption; mechanism; phosphorus; tropical soil; isotherm

1.   Introduction

Soil is an important plant medium that is made of various components and an important resource that influences agricultural production. Plants, just as other living organisms require food for growth, development and reproduction [1]. The burgeoning population has increased demand for food, threatening agriculture production in the coming decades. Soil fertility decline due to mismanagement of plant nutrients further exacerbates the arduous task of satisfying the increasing food demands by the growing population [2]. Primary nutrients such as nitrogen (N), phosphorus (P) and potassium (K) are required in very large quantities by most crops. The three primary nutrients (nitrogen, phosphorus and potassium), which constitute the basic components of most inorganic NPK fertilizers, but whereas nitrogen and potassium are often readily available to plants, P is frequently not so readily available to plants [3]. Thus, although phosphorus is one of the most important nutrients to growing crops, it is also one of the limiting plant nutrients in most Sub-Saharan African (SSA) soil. The factors which account for low P availability in SSA soils include low inherent P content in the parent material from which the soils were derived, and/or depletion of soil reserve P through intensive cultivation, without adequate external P input additions [4]. Phosphorus deficiency reduces crop yields as it is an essential constituent of cell membranes, plant genetic material, and also required for energy storage and transport processes in plant cells for chemical reactions. Therefore, the initial growth stages of plants are predominantly dependent on P due to its role in cell division and development. Plant roots can take up water-soluble P from soil solution [5] mainly through the processes of root interception and diffusion. The diffusion rate of P depends on P concentrations in the soil solution. The amount of P in soil solution highly influences the rate at which it moves. Hence, an adequate amount of P is required to enhance its movement and plant uptake. The soil's buffering potential for P, which is dependent on the proportion of total P in the soil solution also defines the soil's ability to sorb P [1].

P Adsorption, defined as the net accumulation of P at the interface between the soil's solid and water-soluble phases, is determined by the availability of native soil P and the amount of P applied to soils as fertilizers [6]. When soluble P compounds are applied to the soil, they undergo a series of complex reactions that can reduce P availability to crops. Thus, P compounds often react rapidly with other soil minerals by precipitation reactions and adsorption onto the soil's solid particle surfaces. Adsorption reaction is one of the principal processes involved in the retention of P on soil surfaces [6].

In tropical soils, plant P uptake is very low, which is reflected in the low recovery P-fertilizer rates of 5 to 25% [7]. There is, therefore, an urgent need to increase the efficiency of P-fertilizer recovery in low P tropical soils to avoid recalcitrant soil P accumulation [8].

In an attempt to enhance soil P recovery, the presence of heavy metals, precipitation, nitrogen, potassium, and sulfur must be taken into account as they can affect the availability of the recovered phosphorus [9].

Depending on the capacity of the soil to replenish the soil solution P, the P removed from the soil solution by plant root needs to be replaced. The P removed from the soil solution can be replaced through desorption of sorbed P, P released from soil organic matter through microorganisms driven mineralization of soil organic matter or added organic inputs, and application of fertilizer to the soil [10]. According to Guedes et al. [11], adding organic matter to tropical soils can be an efficient strategy to optimize P fertilization by reducing P sorption and enhancing sorbed P reversibility in soils. Among the

factors that influence P availability in tropical soils, sorption and desorption due to variable surface charge characteristics of soil components are considered as the most important factor [11,12].

Bolland et al. [10] reported that the P concentration in soil solution (intensity factor) and the capacity of the soil to replenish the soil P in solution need to be considered. The main factors which affect maximum soil P adsorption capacity include pH, clay mineralogy, types of Fe and Al oxide content, particle size distribution, the crystallinity of soil oxide, quality and quantity of organic matter.

P adsorption is likely to increases in tropical soil with low pH and prevalence of kaolinite and Fe and Al oxides in the clay fraction [13]. Although several works have been done on P sorption in tropical soils, there is still the need to provide comprehensive information on P sorption and how soil properties along with sorption models regulate P availability in tropical soils. Thus, this paper aims to thoroughly review phosphorus sorption in tropical soils alongside phosphorus isotherms, mechanisms of phosphorus adsorption, factors affecting P adsorption, soil P requirements as well as P management in a tropical soil.

2. Phosphorus isotherms

Phosphorus is absorbed by plants as primary monobasic phosphate ion ($H_2PO_4^-$), secondary dibasic phosphate ions (HPO_4^{2-}) and phosphate ions (PO_4^{3-}) [14]. Adsorption isotherms can be defined as the equilibrium quantitative relationships between the amounts of adsorbed and dissolved phosphate species at constant temperatures [15]. The reason for studying phosphate sorption isotherms is to better understand the mechanism underpinning the interaction of the phosphate ions with oxides, oxyhydroxides, sesquioxides in soil have been used to measure the adsorption capacity of soils. Generally, adsorption is characterized by fitting the adsorption isotherms and arriving at a mathematical explanation using one or more adsorption equations [1].

The process of adsorption is mostly described through isotherms, that is, functions that connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). The different isotherm models describing the process of adsorption include Langmuir isotherm, Freundlich isotherm, Brunauer-Emmett-Teller (BET) isotherm, Dubinin-Radushkevich and Temkin isotherm [16]. Under field conditions, P requirements for optimal crop yields vary greatly from soil to soil and with the crop, therefore, adsorption isotherm models can be successfully used to estimate P requirements of soil for optimal yield taking into accounts also, the crop requirement and yield [16]. According to Menzies and Lucia [17], concentrations of organic P forms occurring at the surface horizons of most tropical soils vary widely (from 20% to 90% of the total P). Organic P mineralization and immobilization processes are generally analogous to those of nitrogen and sulfur [17]. Menezes-Blackburn [18] reported that decreases in organic P observed in incubation experiments were matched by equivalent increases in acid extractable P concentration. Menzies [17] also noted that the rate of mineralization of organic P, rather than its total amount, was the main factor determining the availability of organic P to plants. Zahedifar et al. [19] reported that phosphorus uptake rate by plants depends on the age of the plant and plant P uptake peaks at a certain age of the plant and starts to decline afterward.

The Langmuir Isotherm defines adsorbent and adsorbent structures where the degree of coverage by adsorbents is limited to one molecular layer. Langmuir first suggested this isotherm in the year 1918 [20]. They further explained that Langmuir model assumed each adsorbate molecule that occupies only one site, has a homogeneous surface, a single molecule occupies a single surface site and adsorption on the surface is localized. Langmuir adsorption equation is general used by soil chemists for

monitoring P adsorption and calculating the crop P requirements since 1957. Following the use of the Langmuir adsorption equation, a straight line should be obtained when the adsorbent balance concentration is plotted against the equilibrium concentration divided by the sum of adsorption per unit adsorbent [21]. The benefit of the Langmuir equation is that it permitted the measurement of maximum adsorption and relative binding energy for P sorption [21]. The linear form of the Langmuir isotherm equation is given as:

$$q_e = \frac{bq_{max}}{1 + bC_e}$$

Where: q_e is the quantity of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}); C_e is the concentration of adsorbate at equilibrium in solution after adsorption (mg l^{-1}); q_{max} is the maximum adsorption capacity (mg g^{-1}); b is the Langmuir adsorption equilibrium constant (mg l^{-1}).

The essential characteristics of the Langmuir isotherm can be addressed in terms of a dimensionless equilibrium parameter (R_L) [22].

$$RL = \frac{1}{1 + KlC_o}$$

If $R_L > 1$ means unfavorable adsorption, $R_L = 1$ means linear adsorption, $0 < R_L < 1$ means favorable adsorption and $R_L = 0$ means irreversible adsorption.

The Freundlich Isotherm equation is one of the adsorption isotherms which is popularly used to describe the adsorption of organics from aqueous streams onto activated carbon [22]. The Freundlich equation is generally considered strictly empirical but was extensively used to explain soil adsorption of phosphate [23,24]. The Freundlich isotherm linear form of the equation is expressed as:

$$x/m = k.P^{1/n} \ (n > 1) \text{ or } x/m = k.C^{1/n} \ (n > 1)$$

where: x is the mass of the gas adsorbed on mass m of the adsorbent P is pressure; C is the equilibrium concentration of adsorbate in solution; k and n are constants. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$logq_e = log K_f + \frac{1}{n}logP_e \text{ or } logq_e = log K_f + \frac{1}{n}logC_e$$

where: q_e is the extent of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}); P_e is the equilibrium pressure of adsorbent in solution after adsorption; C_e is the equilibrium concentration of adsorbent in solution after adsorption (mg l^{-1}); K_f is the Freundlich constant indicating adsorption capacity and n representing empirical constant.

Regarding monolayer adsorption, the Langmuir adsorption model is the most widely accepted as one type of adsorption sites are viewed to exist on the surface of the adsorbent [25]. Where the Langmuir model was used in other experiments, such as gas-liquid-phase adsorption, two types of sites were considered and a relationship between the concentration of equilibrium and the amount of adsorbate was developed [25]. Since the Langmuir equation describes adsorption on homogeneous surface, the distribution of gaussian energy is used to adjust monolayer adsorption theory to surfaces which are heterogeneous [25].

The most commonly used isotherm for gaseous adsorbate for surface probing is the Brunauer-Emmett-BET analysis is conducted at the boiling temperature of N_2 (77 K). The BET linear equation is given as: $(P/P_o)/Q((P/P_o)-1) = 1/kQ_m + (k-1/Q_mk) (P/P_o)$. Where: P and P_o are the equilibrium and the

saturation pressure of adsorbates at the temperature of adsorption, Q (in moles) is the amount adsorbed on 1g of adsorbent and Qm is the monolayer adsorption capacity and k is the BET constant.

Dubinin-Radushkevich (D-R) Adsorption Isotherm is a very useful empirical theory which allows for the estimation of the amount of gas adsorbed in a microporous sorbent. This equation was proposed by Dubinin, Polanyi and Radushkevich in the year 1947. The theory was based on a pore filling model [26]. Langmuir and Freundlich isotherm constant do not suggest anything regarding the adsorption mechanism but D-R isotherm helps to determine the adsorption mechanism. The linear form of the (D-R) isotherm equation is given as: $\ln Q_e = \ln Q_m - \beta \varepsilon^2$, Where: Q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), Q_m is the maximum adsorption capacity of adsorbent (mg g^{-1}), β is the constant related to adsorption energy, ε is the Polanyi potential (kJ^{2}mol^{-2}). The ε parameter is calculated from: $\varepsilon = RT \ln (1+1/C_e$, where; R is the gas constant, T is the temperature in (K), C_e is the concentration of adsorbate at equilibrium in solution after adsorption(mg l^{-1}), The experimental data can be evaluated by plotting $\ln Q_e$ against ε^2. The value of Q_m and β are estimated from the intercept and slope respectively [27].

Temkin Adsorption Isotherm is another empirical equation that is proposed originally by Temkin. Temkin and Pyzhevwere consider the influence of indirect adsorbing and adsorbing interactions on the isotherms of adsorption. The adsorption heat of all the molecules in the layer will be decreased linearly with coverage due to adsorbing and adsorbing interactions [28]. The Temkin isotherm linear of the equation is expressed as: $q_e = B_T \ln K_T + B_T \ln C_e$, where; K_T is the equilibrium binding constant (mg l^{-1}), BT is the heat of adsorption (Tempkin constant) (Jmol^{-1}), bT is the Tempkin isotherm constant related to the variation of adsorption energy (J mol^{-1}). BT = RT/b_T; R is the gas constant (8.314 JK^{-1}mol^{-1}), T is the temperature (K) [27].

3. Factors affecting phosphorus adsorption

3.1. The physicochemical character of the adsorbent

The properties of the adsorbent that affect its behavior in interactions with the adsorbent are primarily related to the area and surface configuration and the magnitude, distribution and strength of the surface electrical field [29]. Since adsorption reactions involve interactions on surfaces, the surface area of adsorbents is one of the most significant properties. Iron and Aluminium oxides are effective adsorbents of phosphate but aluminum oxides are more effective than iron oxides [30]. He further explained that oxalate extractable aluminum oxides (Al$_{ox}$) adsorb nearly twice as much phosphate as oxalate-extractable iron oxides on per mole basis. According to Bolon et al. [5], it can be due to a lower crystallinity of the aluminum oxides (higher specific surface area) relative to iron oxides and also to a higher load on the former. In terms of synthetic oxides, phosphate amounts adsorbed per m^2 seem to be higher for aluminum oxides than for iron oxides, although the trend is weak [5,30]. The main reason for the differences observed in the capacity of adsorption is due to the differences in crystallinity [31]. Asomaning [30], stated that the conditions in which the soil is formed are determined by the reactivity of the oxides Al and Fe. Under cold, humid, and nutrient-poor conditions, which cause accumulation of organic matter, poorly crystalline oxides of small particle size are preferred, while larger, well-developed crystals are produced under well-aerated tropical conditions [30,32]. The poorly crystalline oxides Al and Fe with the smallest particle size would be the most reactive since the reactivity depends

on the particular surface area [30]. Kaolinites with varying levels of sesquioxides are often dominant in the clay mineralogy of heavily weathered soils [33].

3.2. Soil reaction

This function of the clay-water system affects both the adsorbent and adsorbent properties. The pH of the soil solution defines the degree of dissociation or association of adsorbents, the exact extent of which is a function of the pKa's actual value [34]. If a compound is present in the molecular, cationic, or anionic form may, therefore, affect the degree and magnitude of the adsorption and the intensity by which it is retained, because the energy of adsorption may greatly differ between the dissociated and the associated type [34]. Adsorption on the strongly acid hydrogen-montmorillonite pH 3.35 occurred to the greatest degree relative to the nearly neutral sodium-montmorillonite pH 6.8 [35]. The extent of adsorption of organic compounds with dramatically different chemical characteristics is calculated by three factors: pH of the clay framework, water solubility and continuous dissociation of the adsorbent [35]. The adsorption of acidic-type compounds depended on the pH of the suspension while the adsorption of a simple compound depended on the acidity of the air. Adsorption pH dependency does not extend uniformly to both adsorbents and adsorbents. It would suggest that adsorption is not due to coulombic forces but to van der Waals. The degree of chloroxuron adsorption by various soils was pH-independent [36].

3.3. Surface acidity

It has been known for some time that the activity of protons in the bulk suspension (i.e., as determined by pH) and the activity of protons at or near the colloidal surface (i.e., the acidity in the interfacial region) that differ drastically [37]. Surface acidity as applied to soil systems is the acidity at or above the colloidal surface and represents the system's ability to behave as both a Bronsted and Lewis acids. This is a hybrid term that represents both the total number of acid sites as well as their relative acidity [38]. Surface acidity is perhaps the most critical property of the soil or colloidal system to determine the degree and nature of the adsorption and desorption of basic organic compounds, and whether acid-catalyzed chemical degradation occurs [37]. There is ample evidence, primarily from research, that simple chemical compounds are protonated, both by clays where hydrogen and aluminum are the predominant exchangeable cations and also by intermediate, alkaline and alkaline metal cations [34]. The presence of NH_4^+ was assumed to be a result of the interaction of NH_3^+ with dissociated protons on the exchangeable cations and interlamellar silicate surfaces from residual water. The value of this adsorption mechanism and its complete contribution to the overall adsorption range for clay minerals of the form montmorillonite will depend on the pKa of the adsorbent and the origin of the aluminum-silicate negative charge [34]. The point of zero charges (PZC), which is often equated to pH_0 is an important parameter used to describe variable-charge surfaces [39]. According to Moghimi, et al. [40], pH_0 often coincides with PZC in soils dominated with variables charges PZC may differ considerably from pH_0, but for systems where permanent and variable charges co-exist incomparable magnitude. Moghimi, et al. [40] further explained that soils with a high amount of permanent negative charge have lower PZC values than pH_0 and vice versa. For instance, the PZC in the young soils (Entisols or

Inceptisols) is usually lower than its pH_0 while PZC is often higher than pH_0 in highly weathered soils such as Oxisols [41].

3.4. Electrical potential of clay surface

The electrical field resulting from the load-balancing cations is believed to be responsible for the different surface anomalies found in clays, zeolites and other aluminum silicates. It is now becoming clear that soils are more or less solid structures with minimal moisture content and that most of the effects found are in the field of surface chemistry [41]. The magnitude of aluminum-silicate surface fields is caused by the transformation of adsorbed molecules into soil colloids. Various chemical reactions induced by this high acidity include decomposition of amines, decomposition of $Co(NH_3)_6^{3+}$ into N_2, $Co(OH)_2$, NH_3 and NH_4^+, protonation of amines etc [25].

3.5. Temperature

The processes of adsorption are exothermic and desorption processes are endothermic, so an increase in temperature will usually minimize adsorption so benefit the desorption process [43]. This leads to a weakening of the attractive forces between the solvent and the solid surface (and between adjacent adsorbed solvent molecules) with increasing temperature, and a related increase in solvent solubility. Temperature by its impact on solubility and vapor pressure may influence sorption. In general, a rise in temperature results in lower sorption; however, there are cases where the impact of temperature on solubility is such that higher adsorption occurs at higher temperatures [44].

4. Mechanisms of adsorption

The term sorption is used to explain all the mechanisms resulting in the removal of phosphate from soil solution which is mainly by precipitation and surface adsorption [30,45]. The adsorption of phosphate from solution by clay minerals and pH, concentration and temperature are important in determining the adsorption of phosphate [46]. Differences of opinions have, however, been expressed by various workers regarding how P is fixed by the soils. It is suggested that probably three separate mechanisms, which possibly overlap each other, are responsible for P fixation [47]. At pH 2 to 5 the retention of P is chiefly due to the gradual dissolution of Fe and Al oxides which are reprecipitated as phosphates. At pH 4.5 to 7.5, P is fixed on the surface of the clay minerals and at pH 6 to 10, P is precipitated by the divalent cations. No single mechanism is responsible for P fixation in all soils. Different theories have been postulated to explain the mechanism of P fixation and are briefly discussed below [47].

Probably the oldest theory of the mechanism of P fixation is that phosphate ions in solution are precipitated, thus, becoming a part of the solid phase. The term precipitated P is limited to those compounds which are formed as chemically homogeneous particles from ions in solution. This definition does not include chemically precipitated layers on the surface of soil constituents [48]. In acid soils, Fe and Al appear to be the most likely soil constituents to fix P by chemical precipitation. When Fe and P are combined in equivalent quantities, minimum solubility occurs between pH 2 and 3 [48]. In the presence of excess Fe, however, there is a tendency to extend the range of minimum solubility to pH

4. When Al and P are combined in equivalent quantities minimum solubility occurs at pH 4 but when Al is in excess, the range of minimum solubility extends from pH 4 to 7 [48]. The Fe and Al silicates and sesquioxides are the primary sources supplying Fe^{2+} and Al^{3+} ions leading to the formation of chemically precipitated Fe and Al phosphates in acid soils [49]. Some workers of P sorption, however, reported that such compounds do not exist in large quantities in soils except in highly acidic soils. In alkaline and calcareous soils, Ca forms a series of compounds with P, ranging (from mono-calcium phosphate to hydroxyapatite). P added to calcareous soils, is converted to di-calcium phosphate, then to tri-calcium phosphate, octo-phosphate and finally to hydroxyapatite [49] with the Hydroxyapatite being the only stable P compound in the transition. It is suggested that part of the calcium phosphate combinations existing in soils is of unknown composition and that phosphate and lime exist in a series of combinations, resulting in an apatite structure [50].

It is considered that in calcareous soils the P of low solubility is a carbonate phosphate compound in which one mole of calcium carbonate is combined with three moles of the calcium phosphate. Some other workers opined that some of the superphosphate incorporated into limed soils will ultimately be reverted to fluorapatite similar to rock phosphate in characters [50].

According to this theory, P is fixed by adsorption between the liquid and solid phase of the soil system. The phosphate ions penetrate the liquid-solid interface to form new compounds with the hydrated minerals. The phosphate ions are held tightly by the minerals and non-diffusible structural to form units colloid bound P [50]. The phosphate ions in the diffusable ion atmosphere held as compensation to ions of opposite charges are considered solid bound P. These two forms of bindings are named as micellar binding in contrast to extra-micellar bindings in precipitation theory, both being outside the soil micelles. Phosphorus adsorption reactions can further be classified into chemical and physical adsorption. In chemical adsorption, the phosphate ions react mostly with Fe, Al and Ca on the clay surface and form Fe, Al and Ca hydroxy phosphates [51]. The adsorption of P on the surface of the clay minerals without involving any chemical reaction is considered as physical adsorption. Both types of P adsorptions may be characterized by Freundlich or by Langmuir adsorption isotherms. Fixation of P by kaolinite from dilute P solutions obeyed the Freundlich adsorption isotherm and increased with temperature. Adsorption reaction is certainly involved in P fixation by soils and clay minerals but it may not be the only mechanism to explain the phenomenon of P fixation [50].

According to Asomaning [30], specific adsorption of ions can occur unto uncharged adsorbents and sometimes even unto surfaces bearing a charge of the same sign as the adsorbent. Thus, phosphate can be adsorbed unto surfaces of variable-charge minerals such as aluminum and iron oxides even at alkaline pH, where these adsorbents are negatively charged. Specific adsorption is characterized by the formation of inner-sphere complexes, where no water molecules are linked between the adsorbent and the adsorbate. The most important variable-charge minerals in the soil that adsorb P include aluminum oxides and iron oxides [30]. The maximum adsorption capacity (MAC) of Soil P is regulated mainly by soil pH, particle size distribution, clay mineralogy, soil organic matter content, Fe and Al oxide contents and types, and soil oxide crystallinity [50]. Regarding tropical soils, increased P adsorption has been attributed to other factors including lower pH and predominance of kaolinite and Fe and Al oxides in the clay fraction [45]. The two important factors in controlling adsorption of phosphate ions by iron oxides are self-aggregation and porosity of soil [30]. According to Pena and Torrent [52], the formation of iron phosphate coatings has, however, been rejected by others. These authors rather attributed migration

(diffusion) of phosphate into aggregated iron oxides, particularly ferrihydrite, to be responsible for the slow reaction.

5. Phosphorus requirement of soil

P in soil occurs in various chemical forms which include organic and inorganic P. The main forms of inorganic P in the soil are $H_2PO_4^-$ and HPO_4^{2-} which are also the available forms to plants. However, these ions have the propensity to be adsorbed onto the surface of solid matrices in the soil, resulting in their unavailability to plants. These P forms differ in their behavior and fate in soils. Inorganic P forms are estimated to between 35% to 70% of total P in soil [53]. Primary phosphate minerals such as apatites, strengite, and variscite are very stable. These primary minerals are released into the soil as a result of weathering activities. The secondary phosphate minerals including calcium (Ca), aluminum (Al) and iron (Fe) phosphates, depending on the size of mineral particles and soil pH, have demonstrated varying dissolution rates [54].

As the soil pH increases, the solubility of Fe and Al phosphates increases to pH maxima of 8 whiles the solubility of Ca phosphate decreases at this same pH. Desorption reactions allow the release of P adsorbed into different clays and Al/Fe oxides. Both of these types of P exist in complex balance, ranging from very stable, sparsely distributed to plant-based P pools such as labile P and solution P [53].

For acidic soils, Al/Fe oxides and hydroxides such as gibbsite, hematite, and goethite can dominantly adsorb P. P is first adsorbed on the surface of clay minerals and Fe/Al oxides through the formation of various complexes including monodentate, bidentate and tridentate. At a soil pH of 4 to 9, both protonated and non-protonated forms of bidentate complexation on the surface may occur with protonated bidentate inner-sphere complexation being predominant in acidic soil [53,55,56]. Clay minerals and Fe/Al oxides have broad, unique surface areas, providing a large number of sites for adsorption. Through ionic strength, the adsorption of soil P can be increased. Further chemical reactions may cause P to occur infrequently occurring nanopores in Fe/Al oxides and thus become inaccessible to plants [55].

For calcareous and neutral soils, precipitation reactions dominate P retention, while P may also be adsorbed on the $CaCO_3$ and clay minerals surfaces [57]. Phosphate can precipitate with Ca which produces dicalcium phosphate (DCP) that is available to plants. Dicalcium phosphate can be transformed into various stable forms such as octocalcium phosphate and hydroxyapatite (HAP), which are less available to plants at alkaline pH between 7 to 14, both octocalcium phosphate and hydroxyapatite are less available to plant [55]. More than 50% of total inorganic P in calcareous soils from long-term fertilizer experiments are as a result of HAP. As the soil pH decreases, HAP dissolution increases [53].

Organic P constitutes about 30% to 65% of the total P in soils [5]. Soil organic P occurs primarily in two forms, either in stable forms (inositol phosphates and phosphonates) or inactive forms (orthophosphate diesters, labile orthophosphate monoesters, and organic polyphosphates). The organic P can be released in combination with phosphatase enzyme secretion via mineralization processes facilitated by soil organisms and plant roots [58]. These processes are highly affected by soil moisture, temperature, physical-chemical surface properties, soil pH and Eh (redox potential). Organic P-transformation significantly affects the overall bioavailability of P in soil. As a result, the availability of

soil P is very complex and needs to be assessed systematically, as it is extremely correlated with P dynamics and transformation between different P pools [59].

6.   Improving P solubility in tropical soil

The second most growth-limiting macronutrient after nitrogen is phosphorus. Proper P management in soil contributes significantly to sustainable crop production. Many factors including soil pH, texture, type of clay minerals, calcium carbonate, and organic matter and Mg/Ca ratio of irrigation water significantly influence P availability, P use efficiency and fertilizer P recovery. However, low soil pH and low soil organic matter contents are the major limitations to P availability or solubility in tropical soil [60]. Low soil pH decreases hydroxyl–ion activities, which increased the formation of iron and aluminum phosphate, resulting in low concentrations of soluble P and/or reduced solubility of organic and inorganic P forms in highly weathered soils. Fertilization practices such as the addition of organic manure, crop residues, rock phosphate and water-soluble P fertilizers as well as the incorporation of phosphorus solubilizing organisms that increase soil pH and organic matter content are highly recommended to increase P solubility and availability in highly weathered soil [61].

Organic matter formed from organic manure application increases the available P in the soil as the organic matter increases the negative charges on the surfaces of soil with variable charges [1]. Furthermore, organic matter contains negatively charged functional groups such as carboxyl and phenol which interact with Al^{3+}, Fe^{3+} to reverse P complexation with Al^{3+}, Fe^{3+}, and thereby increasing P availability in the soil [1]. The organic acids released following the addition of the manure compete more effectively for adsorption sites and decrease P sorption in highly weathered soil.

Rock phosphate is a natural P mineral rock used as a phosphatic fertilizer, animal feed supplement and an industrial chemical [62]. RP is characterized by slow release of P, therefore applying RP together with P solubilizing microbes enhances solubilization of RP. P solubilizing microbes can stimulate P release from RP because they produce organic acids during their metabolic activities [63,64]. Due to the predominance of Al^{3+}, Fe^{3+} in highly weathered soil, Phosphates from applied P fertilizers can be fixed as free oxides and hydroxides of aluminum and iron, which are unavailable to plant [65]. Application of P solubilizing microbes (such as bacterial and fungi) can solubilize inorganic P fertilizers when incorporated into the soil [66].

Crop residues have been reported to increased P availability in tropical soil [67]. If crop residues left in the field are incorporated in the soil, the contained in them can be recycled but if the crop residues are fed to livestock, the P in them can be only be returned to the soil through manure or bone meal. The amount of P released from crop residues into the soil depends on the concentration of P in the crop residues. However, crop residue released from P into the soil can be mineralized or immobilized. Microbial P immobilization occurs when the total P content of the crop residue is not enough to compensate for the P requirement of the microorganisms [68,69]. Net mineralization of organic P occurs through the action of microorganisms and phosphatases and phytases exudates from plants [70]. Also, decomposition of crop residues can increase soil pH and soil organic matter, leading to decreased P sorption [70].

7.   Phosphorus management in tropical soil

Sustainable crop production aims at maintaining high crop yield without adversely affecting ecosystems' ability to meet the need of current as well as future generations [71]. Since phosphorus in agriculture is the second most growth-limiting macronutrient after nitrogen, its proper management in soil contributes significantly to sustainable crop production. In such soils where yield is limited because of inherent low P concentration (P deficient soils), application of the relatively higher amount of mineral P fertilizers is the only way to enhance soil available P status to a target value in a long run that can sustain high crop yield [67]. However, once the target value is reached, the available soil phosphorus concentration can be kept at a level that can sustain high crop yield through maintenance fertilization (replacing only the P removed from the field along with the harvested crops).

The P contained in crop residues left in the field can be recycled by incorporating the residues into the soil whereas part of P in crop residues fed to livestock can be returned to the soil in the form of manure and also as bone meal [67]. The mineralization of such organic P sources can occur through the action of microorganisms and plants exuding phosphatases and phytases. However, the P removed along with cereal grains, other edible vegetable parts and livestock products such as cow dung, milk and meat used for human consumption need to be replaced through mineral P fertilizer application [71]. Therefore, under the condition where P removed from the soil by harvested crops can be returned as crop residues and manures, the amount of mineral P fertilizer required for maintenance fertilization becomes less.

In a nutshell, regular application of maintenance P fertilizers, incorporation of crop residues and application of organic manures can reduce nutrient mining and contribute to sustainable crop production [67]. Continuous applications of P fertilizer to meet plant needs for their growth and development can lead to a significantly large reserve of residual P (P legacy) in soils, but this is not readily available to plants [72]. P legacy represents the cumulative P that has been added to soils by fertilizers and manures minus P removed in harvested crops and run-off and leaching [73]. Excess P buildup in the soil raises ecological and environmental concerns since the presence of excess soluble P affects water quality, biodiversity and human health [74,75].

According to Sattari et al. [76] between 2005 and 2007, global accumulation of legacy P in soil stood at 550 kg P ha^{-1}, and that projected global crop demand for P will increase to about 11.8 kg P ha^{-1} (ca. 18 11.8 P year^{-1}) in 2050. Based on these results, it could be hypothesized that legacy soil P might replace a large fraction of P fertilizer use globally, meeting crop P demands for approximately 9–22 years depending on the availability scenarios.

Table 1. Summarized results obtained from the study.

Sources	Country	Method	Key Findings
Wang and Li [12]	USA	Field and laboratory experiments	For wetland sediments, the relationship between the amount of P adsorbed and the equilibrium P concentration as determined by the Langmuir and linear isotherms was quite similar. The high P adsorption in the marine sediment might be related to an abundance of $CaCO_3$.
Hussain et al. [21]	Pakistan	Field and laboratory experiments	The Freundlich equation parameters (1/n) negatively correlated with CEC and exchangeable $Ca^{2+} + Mg^{2+}$ but positively correlated with $CaCO_3$, clay content and not with other soil properties (pH, EC, ESP, SAR, OM, and TSS). The K_f positively correlated with CaCO3 and SP but not with other properties like pH, EC, CEC, SAR, ESP, OM, exchangeable $Ca^{2+} + Mg^{2+}$ and TSS.
Hadgu et al. [77]	Ethiopia	Field experiment and laboratory analysis	The Langmuir and Freundlich adsorption models are robust in predicting P adsorption in the soils. Soil properties like clay, sand, CEC and $CaCO_3$ contents influence P adsorption.
Tamungang et al. [78]	Cameroon	Fieldwork and Laboratory analysis	The adsorption isotherms showed different curves for each of the soil tested.
Maluf et al. [79]	Brazil	Laboratory analysis	Humic acid rates and carbonate sources affected phosphorus adsorption in Oxisol and Entisol.
Ayenew et al. [80]	Ethiopia	Field experiment	The Freundlich model could be considered as the best model for the description of the P adsorption characteristics of the soils in this particular study area. The Freundlich coefficient K_f (adsorption capacity) value ranged from 123.32 to 315.31 mg P kg^{-1} and depended on the amorphous form of Fe and Al.

Continued on next page

Sources	Country	Method	Key Findings
Mihoub et al. [81]	Algeria	Field experiment and laboratory analysis	Calcium carbonate is considered to be the major reason for P unavailability to plants by adsorption and precipitation reactions. Use of Freundlich P sorption isotherm, which relates soil solution P concentration with the quantity of P adsorbed in soil, to predict P fertilizer requirement of a specific soil is a better approach rather than using soil test.
Anjembe et al. [82]	Nigeria	Laboratory and pot experiments	Variations in P adsorption between the soils could have been due to various reasons such as the initial P contents of the soils, their clay contents which could have provided the active sites for the adsorption, the organic matter content etc.

8. Conclusion

The review was done to explore literature that reported about phosphorus adsorption in soils, management and adsorption isotherms. The findings were that Langmuir and Freundlich adsorption models are robust in predicting P adsorption in the soils (tropical soils). In tropical soils, P adsorption can be influenced by some soil properties such as sand, clay, $CaCO_3$ and CEC. The findings from the review indicated that by using adsorption isotherms, different curves generated for each soil tested. The review also showed that Freundlich model could be considered as the best model for the description of the P adsorption characteristics of the soils. In concluding, the review provided adequate evidence that P is fixed and absorbed in soils with pH ranging "between" 4.5 to 7.5 and also between liquid and solid phase of the soil.

Conflict of interest

The authors declare there is no conflict of interest.

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