Phosphorus adsorption in tropical soils: a critical review

Hanyabui E[1*], Apori O. S[1], Abindaw T[1], Asiamah Y. J[2], and Ali M[3],

[1] Department of Soil Science, School of Agriculture, University of Cape Coast, Ghana.

[2] Department of Molecular Biology and Biotechnology, School of Biological Sciences, University of Cape Coast, Ghana.

[3] Department of Crop Science, School of Agriculture, University of Cape Coast, Ghana.

*Corresponding author's email: emmanuel.hanyabui@stu.ucc.edu.gh

Abstract

In tropical soils, phosphorus adsorption is a major key process that controls its availability to crops. Phosphorus is one of the main essential plant nutrients require by plant in large quantities. Plants absorb P either as the primary monobasic phosphate, $H_2PO_4^-$ ions or smaller amounts of the secondary dibasic phosphate, HPO_4^{2-} ions and the phosphate ion, PO_4^{3-}. Inadequate supply of phosphorus to the plant affect its potential yield nor cannot complete reproductive cycle. Regardless of its importance to crop, it can also reduce more than 40 % of crop yield of the world's cultivated land. Additionally, P levels in tropical soil are been depleted at a higher rate and according to some estimate from the literature reviewed there will be no P reserve in soil by the year 2050. Phosphate adsorption isotherm study the interaction of the ions with the oxides and soil and also measure the adsorption capacity of soils. Application of P to crop in the form of fertilizers can be adsorbed by the soil but may not be available for plants restricted with specific adaptations. Application of P containing fertilizers can increase available P in the soil hence increase crop yield which can be used to feed the world's rapid population growth.

Keywords: Adsorption, mechanism of adsorption, phosphorus, phosphorus management in tropical soil, phosphorus adsorption isotherm.

Introduction

Soil is an important plant medium which is made of various components and factors that contribute to the yield of agricultural production. With regard to other living organisms, plants need food for their growth, development and reproduction (Njoyim et al., 2016). Over population has resulted into increase in demand for food in a sustainable manner which is the challenge for agriculture in the coming decades. Soil fertility decline is as a result of mismanagement of plant nutrients making the task very difficult. (Yaser and Rahim, 2013). In terms of nutrient supply, it is base on the essentiality of plant nutrients to a particular soil type. Mostly, primary nutrient which includes Nitrogen, Phosphorus and Potassium are being used. The three primary nutrients which includes Nitrogen, N, Phosphorus, P and Potassium, K constitute the N:P:K fertilizer but N and K are readily made available to plants whereas P is most at times unavailable to plants (Tening et al., 2013). Phosphorus is one of the most important limiting nutrients in most soils of Sub-Saharan Africa (SSA). This could be due to low P content in the parent material from which the soils were derived, and/or due to depletion of soil reserve P through intensive cultivation, without adequate external replenishment (Wolde and Haile, 2015). Phosphorus is an essential plant nutrient and its deficiency tends to limit plant growth. In the tropics, phosphorus is often the most limiting plant nutrient, primarily due to the challenges encountered in the management of phosphorus (Njoyim et al., 2016). Phosphorus (P) is an important component of cell membranes, plant genetic material and also for energy storage and transfer systems for chemical reactions in plant cells. Plant growth at the initial stage is particularly dependent on P because of the needs for rapid cell division and expansion. Plant root can only take up water-soluble P from soil solution (Bolland et al., 2001; Silva and Uchida, 2000). In moist soil, as the roots grow through the soil, plant roots intercept P and moves through the soil solution to the roots by

diffusion. The proportion of the P in solution depends on the rate of diffusion. The smaller the proportion, the slower it moves and so the more P is required to give an adequate rate of P supply. The buffering capacity of the soil for P depends on the proportion in solution, which determines the capacity of the soil to sorb P (Njoyim et al., 2016).

Adsorption is the net accumulation of chemical species at the interface between a solid phase and an aqueous solution phase which determine availability of native soil P and the rate of P applied to soils in fertilizers (Pierzynski et al., 2005). When soluble P compounds are applied to the soil, they undergo a series of complex reactions which lead to the decline of the availability of the P added to the soil. The compounds react rapidly with 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 (Pierzynski et al., 2005.

In tropical soils, P uptake by plant is very low since the recovery rates of P-fertilizer range from 5 to 25 %. Low P-fertilizer recovery is due to the specific phosphate adsorption, which is not often returned to soil solution in highly weathered soils preventing P uptake by plants (Maluf et al., 2018). Depending on the capacity of the soil to replenish the 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 from nearby sources, P released from soil organic matter as a result of the activity of soil organisms on the organic matter and application of fertilizer to the soil. The concentration of P in soil solution (intensity factor) and the capacity of the soil to replenish the soil P in solution need to be considered (Bolland et al., 2001).

Soil P maximum adsorption capacity (PMAC) is affected mainly by various factors such as soil pH, particle size distribution, clay mineralogy, Fe and Al oxide contents and types, and soil oxide crystallinity. Taking other factors into consideration, in tropical soil there is an increased in P adsorption due to lower pH and predominance of kaolinite and Fe and Al oxides in the clay fraction (Fink et al., 2014). However, there is little information on P adsorption in tropical soils, thus the objective of this review is to address phosphorus adsorption in tropical soils under the following thematic areas; phosphorus isotherms, mechanisms of phosphorus adsorption, factors affecting P adsorption, P requirement of soil and also P management in tropical soil.

Phosphorus isotherms

Plants absorb P either as the primary monobasic phosphate, $H_2PO_4^-$ ions or smaller amounts of the secondary dibasic phosphate, HPO_4^{2-} ions and the phosphate ion, PO_4^{3-} (Conklin, 2005). Adsorption isotherms can conveniently be described as the equilibrium relationships between the amounts of adsorbed and dissolved species of phosphate at constant temperature in quantitative terms (Khan et al., 2010). Phosphate adsorption isotherms are important criteria to study the interaction of the ions with the oxides and soil and have been used to measure the adsorption capacity of soils. Adsorption is usually characterized by fitting the adsorption isotherms and their mathematical description using one or more adsorption equations (Njoyim et al., 2016).

The process of adsorption is mostly described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). The different isotherms models describing process of adsorption included Langmuir isotherm, Freundlich isotherm, Brunauer-Emmett-Teller (BET) isotherm, Dubinin-Radushkevich and Temkin isotherm (Jamal et al., 2018). Under field conditions, P requirements for optimal crop yields vary greatly from soil to soil and with crop, therefore, adsorption isotherm models can be successfully used to estimate P requirements of soil for optimal yield (Jamal et al., 2018).

The Langmuir Isotherm describes adsorbate and adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer. This isotherm was proposed originally by Langmuir in the year 1918 (Thajeel et al., 2013). The Langmuir model assumed each adsorbate molecule which occupies only one site, has a homogeneous surface, a single molecule occupies a single surface site and adsorption on surface is localized (Thajeel et al., 2013). Langmuir adsorption equation is general used by soil chemists for monitoring P adsorption and calculating the crop P requirements since 1957. After using the Langmuir adsorption equation, a straight line is supposed to be obtained when equilibrium concentration of adsorbate is plotted against equilibrium concentration divided by amount of adsorption per unit adsorbent (Hussain at al., 2003). The advantage of the Langmuir equation is that it made possible to calculate an adsorption maximum and a relative binding energy for P sorption (Hussain at al., 2003). 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 (mgg^{-1}); C_e is the concentration of adsorbate at equilibrium in solution after adsorption (mgl^{-1}); q_{max} is the maximum adsorption capacity(mgg^{-1}); b is the Langmuir adsorption equilibrium constant (lmg^{-1})

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (Surchi, 2011).

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

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

The Freundlich Isotherm equation is one of the adsorption isotherms which is popularly used to describe adsorption of organics from aqueous streams onto activated carbon (Surchi, 2011). The Freundlich equation is normally considered to be purely empirical in nature but has been used extensively to describe the adsorption of phosphate by soils (Aslam et al., 2000; Arshed et al., 2000). The linear form of the Freundlich isotherm equation is given 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 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:

$$\log q_e = \log K_f + \frac{1}{n}\log P_e \text{ or } \log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where: q_e is the extent of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mgg^{-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 (mgl^{-1}); K_f is the Freundlich constant indicating adsorption capacity and n represent empirical constant.

Brunauer- Emmett- Teller (BET) isotherm is the most commonly used gaseous adsorbate for surface probing. BET analysis is conducted at boiling temperature of N_2 (77 K). Other probing adsorbents include argon, carbon dioxide and water. 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 allow one to calculate 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 (Keller & Staudt, 2005). Langmuir and Freundlich isotherm constant do not suggest anything regarding adsorption mechanism but D-R isotherm helps to determine the adsorption mechanism. The linear form of the (D-R) isotherm equation is given as (Chowdhury et al., 2010): $\ln Q_e = \ln Q_m - \beta\varepsilon^2$, Where: Q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mgg^{-1}), Q_m is the maximum adsorption capacity of adsorbent (mgg^{-1}), β is the constant related to adsorption energy, ε is the polanyi potential (kJ^2mol^{-2}). The ε parameter is calculated from: $\varepsilon = RT1n\,(1+1/C_e$, 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(mgl^{-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.

Temkin Adsorption Isotherm is another empirical equation that is proposed originally by Temkin (1935). Temkin and Pyzhevwere take into account the effects of indirect adsorbate and adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate and adsorbate interactions (Tan, 2008; Surchi, 2011). The linear form of the Temkin isotherm equation is given as (Chowdhury et al., 2010): $q_e = B_T \ln K_T + B_T \ln C_e$, where; K_T is the equilibrium binding constant (lmg^{-1}), BT is the heat of adsorption (Tempkin constant) ($Jmol^{-1}$), bT is the Tempkin isotherm constant related to variation of adsorption energy ($Jmol^{-1}$). $BT = RT/b_T$; R is the gas constant (8.314 $JK^{-1}mol^{-1}$), T is the temperature (K).

Mechanisms of adsorption

Phosphate availability in soils is often a limiting factor for plant growth, even though the total amount of soil P may be great. The adsorption of phosphate from solution by clay minerals and pH, concentration and temperature have been shown to be important in determining the adsorption of phosphate (Shen et al., 2011). Differences of opinions have, however, been expressed from time to time by various workers regarding the manner in which P a fixed by the soils. It is suggested that probably three separate mechanisms, which possibly overlap each other, are responsible for P fixation (Sato and Comerford, 2005). At pH 2 to 5 the retention of P is chiefly due to the gradual dissolution of Fe and AI oxides which are reprecipitated as phosphates. At pH 4.5 to 7.5, P is fixed on the surface of the clay particles 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 (Sato and Comerford, 2005).

Probably the oldest theory pertaining to 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 surface of soil constituents (Helfenstein et al., 2018). 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 (Sato and Comerford, 2005). In the presence of excess of 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 whe1e excess of Al is present, the range of minimum solubility extends from pH 4 to 7 (Sato and Comerford, 2005). The Fe and Al silicates and sesquioxides are the primary sources supplying Fe^2 and AI^3 ions leading to the formation of chemically precipitated Fe and Al phosphates in acid soils (Gregor, 2005). Some of the workers, however, reported that such compounds do not exist in large quantities in soils except in highly acid soils. In alkaline and calcareous soils, Ca forms a series of compounds with P, ranging (from mono-calcium phosphate to hydroxy apatite). P added to calcareous soils, is converted to di-calcium phosphate, then to tri-calcium phosphate, octo-phosphate and finally to hydroxy apatite (Gregor, M (2005). The last

one is the only stable compound. It is suggested that part of the calcium phosphate combinations existing in soils are of unknown composition and that phosphate and lime exist in a series of combinations, having an apatite structures. The relation of one with another form of calcium phosphate when subject to pH changes, hydrolysis, and carbonation are shown in the phosphate cycle (Kanwar and Grewal, 1990).

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 held that some of the superphosphate incorporated into limed soils will ultimately be reverted to fluorapatite similar to rock phosphate in characters (Kanwar and Grewal, 1990).

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-diffusable structural units are named colloid bound P (Kanwar and Grewal, 1990). The phosphate ions in the diffusable ion atmosphere held as compensation to ions of opposite charges are considered saloid 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. Another classification of adsorption reaction of P by the soil is that of chemical adsorption and physical adsorption. In the chemical adsorption, the phosphate ions react mostly with Fe, Al and Ca on the clay surface and form Fe, Al and Ca hydroxy phosphates (Dabrowski, 2001). 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 adsorption isotherms or by Langmuir adsorption equation. 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 (Kanwar and Grewal, 1990).

Factors affecting phosphorus adsorption

a. Physicochemical character of the adsorbent

The properties of the adsorbent which influence its behavior in interactions with the adsorbate are primarily related to the area and configuration of the surface, and to the magnitude, distribution, and intensity of the electrical field at the surface (Hatice, 2010).

Since adsorption reactions involve interactions at surfaces, one of the most important properties of adsorbents is their surface area. The 1:1 minerals, primarily those of the kaolin group, because of their low cation exchange capacity and low surface area, have very limited adsorption capacities (Schoonheydt and Johnston, 2011). Because virtually all adsorption is on external surfaces and the extent of these surfaces is so limited, it has not been possible to experimentally observe the interactions on these surfaces of the 1: 1 clays by infrared spectroscopy without resorting to intersalation techniques (Schoonheydt and Johnston, 2011). The 2: 1 minerals which can expand, such as montmorillonite and vermiculite, have very high cation exchange capacities and surface areas (Uddin, 29017). These values are from ten to 100 times greater than those for kaolinite. As a result, the extent of adsorption is sufficiently great to be readily measured and in many cases the spectra of the adsorbed molecules may be observed. The non-expanding 2: 1 minerals, such as illite and chlorite, are intermediate in adsorption capacities between the 1: 1 and expanding 2: 1 clay minerals (Schoonheydt and Johnston, 2011)

The total charge on the surface of minerals is largely due to the extent to which isomorphous substitution occurred in the genesis of the mineral. The intensity of the electrical field at the surface may be affected by the location of the isomorphous substitutions (Jia et al., 2017). In the case of layer lattice silicates, isomorphous substitutions may occur in either the octahedral layer or the tetrahedral layer. The proportion of charges originating in the tetrahedral positions should be related to the fixation of potassium by 2: 1 minerals due to the stronger attractive forces at the clay surface (Jia et al., 2017). The adsorbent may influence adsorption through its effect on the orientation of the adsorbate. This influence may be exerted through a combination of two factors: surface configurations such as the holes in the distorted hexagonal network of surface oxygens in the 2:1 minerals which provide positions for "keying" of molecules and

impose limitations on orientation of the adsorbate, and the attractive forces between adjacent 2: 1 layers may be sufficiently great to cause the adsorbate to be oriented in such a manner as to give a minimum interlayer distance, or to limit adsorption to one layer (Jia et al., 2017).

b. Soil reaction

This property of the clay-water system influences the properties of both the adsorbent and adsorbate. The pH of the soil solution will determine the degree of dissociation or association of adsorbate, the exact extent being a function of the actual value of the pKa (Ajibola et al., 2017). Therefore, whether a compound is present in the molecular, the cationic, or anionic form can affect the extent and magnitude of adsorption and the strength by which it is held, since the energy of adsorption may be vastly different between dissociated and the associated form (Ajibola et al., 2017).

Adsorption occurred to the greatest extent on the highly acid hydrogen-montmorillonite pH 3.35 compared to the near neutral sodium-montmorillonite pH 6.8. The magnitude of adsorption of organic compounds with widely different chemical character is governed by three factors which are pH of the clay system, water solubility and the dissociation constant of the adsorbate (Burgos et al., 2002). The adsorption of acidic-type compounds was dependent upon the pH of the suspension, while the adsorption of a basic compound was dependent upon the surface acidity. pH dependence of adsorption does not universally apply to all adsorbents and adsorbates. This would suggest that adsorption is due to van der waals rather than coulombic forces. The magnitude of adsorption of chloroxuron by different soils was essentially pH independent (López-Velandia et al., 2014).

c. Surface acidity

It has been recognized for some time that the activity of protons in the bulk suspension (i.e., as measured by pH) and the activity of protons at or in close proximity to the colloidal surface (i.e., the acidity in the interfacial region) may differ drastically (Agmon et al., 2016). The term "surface acidity" as applied to soil systems is the acidity at or in close proximity to the colloidal surface and reflects the ability of the system to act both as a Bronsted acid and a Lewis acid. This is a composite term which reflects both the total number of acid sites and their relative degree of acidity (Yang et al., 2007). Surface acidity is probably the most important property of the soil or

colloidal system in determining the extent and nature of adsorption and desorption of basic organic compounds as well as determining if acid-catalyzed chemical degradation occurs (Agmon et al., 2016). There is overwhelming evidence, mainly from infrared studies, pointing to the fact that there is protonation of compounds basic in chemical character both by clays where hydrogen and aluminum are the predominant exchangeable cation and also those saturated with transition, alkaline, and alkali metal cations (Ajibola et al., 2017). The existence of NH_4^+ was thought to be a result of the interaction of NH_3 with protons dissociated from residual water on the exchangeable cations and the interlamellar silicate surfaces. The importance of this adsorption mechanism and its total contribution to the overall order of magnitude of adsorption for montmorillonite-type clay minerals would depend upon the pKa of the adsorbate and the origin of the negative charge in the aluminium-silicate (Ajibola et al., 2017).

d. Electrical potential of clay surface

The electrical field arising from the charge-balancing cations is considered to be responsible for the various surface phenomena observed in clays, zeolites, and other aluminium-silicates. It is now becoming apparent that soils are more nearly solid state systems with a limited moisture content and most of the effects observed are in the domain of surface chemistry (Chen et al., 2016). The magnitude of surface fields of aluminium-silicate surfaces is as a result of the transformation of adsorbed molecules in 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 (Chen et al., 2017).

e. Temperature

Adsorption processes are exothermic and desorption processes are endothermic in nature, and an increase in temperature would normally be expected to reduce adsorption and favor the desorption process (Hlady and Buijis, 1996). This corresponds to a weakening of the attractive forces between the solute and the solid surface (and between adjacent adsorbed solute molecules) with increasing temperature, and corresponding increase in solubility of the solute in the solvent. Exchange reactions tend to be temperature independent (Horsfall and Spiff, 2005). Temperature may influence adsorption through its effects on solubility and vapor pressure. Generally speaking, an increase in temperature leads to decreased adsorption; however, there are

exceptions in which the effect of temperature on solubility is such that increased adsorption occurs at higher temperatures (Horsfall and Spiff, 2005).

Phosphorus requirement of soil

P in soil occurs in various chemical forms which includes organic P and inorganic P. The main forms of inorganic P in soil are $H_2PO_4^-$ and HPO_4^{2-} which are also the available forms to plants. However, these ions can also be adsorbing onto the surface of solid matrices in the soil which make them unavailable to plants. These P forms differ in their behavior and fate in soils. There are about 35 % to 70 % of total P in soil which are Inorganic P (Shen et al., 2011).

Primary P minerals such as apatites, strengite, and variscite are very stable. Through weathering, available P is release from these minerals which are too slow to meet the crop demand though direct application of phosphate rocks. Mineral apatites has showed relatively efficient for crop growth in acidic soils. Secondary P minerals including calcium (Ca), aluminum (Al) and iron (Fe) depending on size of mineral particles and soil pH, phosphates vary in their dissolution rates (Pierzynski et al., 2005; Oelkers and Valsami-Jones, 2008).

As the soil pH increases, solubility of Fe and Al phosphates increases but solubility of Ca phosphate decreases, except soil with a pH values greater than 8. Desorption reactions allow P adsorbed on various clays and Al/Fe oxides to be released. All these P forms occur in complex equilibria with each other, representing from very stable, sparingly available, to plant-available P pools such as labile P and solution P (Shen et al., 2011).

In acidic soils, P can be dominantly adsorbed by Al/Fe oxides and hydroxides, such as gibbsite, hematite, and goethite. P is first adsorbed on the surface of clay minerals and Fe/Al oxides by forming various complexes. At a soil pH of 4 to 9, the protonated and nonprotonated bidentate surface complexes may occur at the same time, while protonated bidentate innersphere complex is predominant under acidic soil conditions (Luengo et al., 2006; Arai and Sparks, 2007; Shen at al., 2011). Clay minerals and Fe/Al oxides have large specific surface areas, which provide large number of adsorption sites. Soil P adsorption can be improved with increasing ionic strength.

Further chemical reactions can make P to be occluded in nanopores that frequently occur in Fe/Al oxides, and thereby become unavailable to plants (Arai and Sparks, 2007).

In neutral to calcareous soils, P retention is dominated by precipitation reactions, even though P can also be adsorbed on the surface of $CaCO_3$ and clay minerals (Devau et al., 2010). Phosphate can precipitate with Ca which produce 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 (Arai and Sparks, 2007). More than 50% of total inorganic P in calcareous soils from long-term fertilizer experiments (H. Li, personal communication) are as a result of HAP. As the soil pH decreases, HAP dissolution increases. Soil P can be mobilized from calcareous soil through rhizosphere acidification (Shen et al., 2011).

Organic P generally contribute to about 30% to 65% of the total P in soils (Condron et al., 2005). Soil organic P mainly exists in two forms, either in stabilized forms (inositol phosphates and phosphonates) or active forms (orthophosphate diesters, labile orthophosphate monoesters, and organic polyphosphates). The organic P can be released through mineralization processes facilitated by soil organisms and plant roots in association with phosphatase secretion (Condron et al., 2005). These processes are highly influenced by soil moisture, temperature, surface physical-chemical properties, and soil pH and Eh (for redox potential). The overall bioavailability of P in soil is highly influenced by organic P transformation. As a result of that, the availability of soil P is very complex and needs to be systemically evaluated because it is extremely associated with P dynamics and transformation among various P pools (Turner et al., 2007).

Phosphorus management in tropical ecosystem.

Sustainable crop production aims at maintaining high crop yield without adversely affecting ecosystems to meet the need of current as well as future generations (Tilman et al., 2002). 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 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 (Balemi and Negisho, 2012). 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 back to the soil in the form of manure and also as bone meal (Balemi and Negisho, 2012). 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 (Tilman et al., 2002). Therefore, under condition where P removed from the soil by harvested crop 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 (Balemi and Negisho, 2012).

Some results obtained from the study are summarized in Table 1 below

Authors (Year)	Country	Method	Findings	Source of Data
Hadgu et al. (2014)	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	Article
Tamungang et al. (2016)	Cameroon	Field work and Laboratory analysis	The adsorption isotherms showed different curves for each of the soil tested.	Journal
Maluf et al. (2017)	Brazil	Laboratory analysis	Humic acid rates and carbonate sources affected phosphorus adsorption in Oxisol and Entisol.	Article
Ayenew et al. (2018)	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 amorphous form of Fe and Al.	Article
Mihoub et al. (2016)	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.	Article
Anjembe et al. (2017)	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.	Journal

Wang and Li (2010)	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 $CaCO_3$.	Article
Hussain et al. (2003)	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.	Journal Article

Conclusion

The review was done to explore literature that reported about phosphorus adsorption in soils, management and adsorption isotherms. What emerged from this review was 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 such as sand, clay, CaCO3 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 this particular area. 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.

REFERENCES

Agmon, N., Bakker, J.H., Campen, R.K., Henchman, H.R., Pohl, P., Roke, S., Thamer, M., and Hassanali, A (2016). Protons and Hydroxide Ions in Aqueous Systems.

Ajibola, A., Adeoye, O.A and Bello, S. O (2017). Adsorption of dyes using different types of clay: review. 7: 543–568

Arai, Y and Sparks, D. L (2007). Phosphate reaction dynamics in soils and soil minerals: a multiscale approach. Adv Agron 94: 135–179.

Arshad, M., Rahmatullah, M. S and Yousaf, M (2000). Soil properties related to phosphorus sorption as described by modified Freundlich equation in some soils. Int. J. Agri. Biol., 2: 290–2.

Anjembe, B., Ibrahim, N.B and Kurayemen, C. (2017). Phosphorus adsorption isotherms of some low activity clay soils as influenced by soil properties and their effect on fertilizer p recommendations and yield of soybean (glycine max (l.) merr.) in benue state, Nigeria. European Journal of Agriculture and Forestry Research Vol.5, No.3, Pp.16-30.

Aslam, M., Rahmatullah, M. S and Yasin, M (2000). Application of Freundlich adsorption Isotherm to Determine Phosphorus Requirement of several Rice soils. Int. J. Agri. Biol., 2: 286–8.

Ayenew, B., Tadesse, A. M., Kibret, K., and Melese, A. (2018). Phosphorous status and adsorption characteristics of acid soils from Cheha and Dinsho districts, southern highlands of Ethiopia. Environ System Research. 7:17, Pp, 2-14.

Balemi, T and Negisho, K (2012). Management of soil phosphorus and plant adaptation mechanisms to phosphorus stress for sustainable crop production: a review. *Journal of Soil Science and Plant Nutrition*, 12 (3), 547-562.

Burgos, D.W., Pisutpaisal, N., Mazzarese, C.M and Chorover, J (2002). Adsorption of Quinoline to Kaolinite and Montmorillonite. 19:59-68.

Bolland, M.D.A., Allen, D.G and Barrow, N.J (2001). Sorption of phosphorus by soils: How it is measured in Western Australia. Western Australian Department of Agriculture, Bunbury, pp: 31

Gregor, M (2005). Mullite-corundum-spinel-cordierite-plagioclase xenolithsin the Skaergaard

Marginal Border Group: multi-stageinteraction between metasediments and basaltic magma. 49: 196–215.

Chowdhury, S., Mishra, R., Saha, P., & Kushwaha, P. (2010). Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. Journal of Desalination, 265, 159-168. http://dx.doi.org/10.1016/j.desal.2010.07.047.

Chen, C. (2016). A mineralogical approach to use the non-qualified fine aggregates in asphalt concrete pavement. Pp, 4-244.

Condron, L. M., Turner, B.L. and Cade-Menun, B. J (2005). Chemistry and dynamics of soil organic phosphorus. In JT Sims, AN Sharpley, eds, Phosphorus: Pp. 245-354.

Devau, N., Hinsinger, P., Le Cadre, E., Colomb, B and Gerard, F (2011). Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils.

Dabrowski, A (2001). Adsorption from theory to practice. 93: 135-224.

Devau, N., Le Cadre, E., Hinsinger, P and Ge´rard, F (2010). A mechanistic model for understanding root-induced chemical changes controlling phosphorus availability. Ann Bot (Lond) 105: 1183 1197.

Environment. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Inc., Madison, WI, pp 87–121.

Fisseha Hadgu, F., Gebrekidan, H., Kibret, K., and Yitaferu, B. (2014). Study of phosphorus adsorption and its relationship with soil properties, analyzed with Langmuir and Freundlich models. Agriculture, Forestry and Fisheries. Vol. 3, No. 1, 2014, pp. 40-51.

Hussain, A., Ghafoor, Anwar-Ul-Haq, A. M and Nawaz, M (2003). Application of the Langmuir and Freundlich Equations for P Adsorption Phenomenon in Saline-Sodic Soils. International Journal of Agriculture and Biology, 3:349–356.

Helfenstein, J., Jegminat, J., McLaren, T.I., and Frossard, E (2018). Soil solution phosphorus turnover: derivation, interpretation, and insights from a global compilation of isotope exchange kinetic studies. 15, 105–114.

Hlady, V and Buijis, J (1996). Protein adsorption on solid surfaces. 7(1):72-77.

Horsfall, M and Spiff, I.A (2005). Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass. (2):163-169.

Hatice, K. (2010). The effects of physical factors on the adsorption of synthetic organic compounds by activated carbons and activated carbon fibers.

López-Velandia, C., Moreno-Barbosa, J.J., Sierra-Ramirez, R., Giraldo, L and Juan Moreno-Piraján, C (2014). Adsorption of Volatile Carboxylic Acids on Activated Carbon Synthesized from Watermelon Shells. Pp, 227-242.

Jia, Z., Wang, Q., Zhu, C and Yang, G (2017). Adsorption of Ions at the Interface of Clay Minerals and Aqueous Solutions. Pp. 96-120.

Jamal, A., Muhammad, D., Rahman, M and Jamal, H (2018). Application of adsorption isotherms in evaluating the influence of humic acid and farmyard manure on phosphorous adsorption and desorption capacity of calcareous soil. An International Scientific Journal, 107: 136-149.

Kanwar, J.S and Grewal, J.S. (1990). Phosphorus fixation in indian soils. Pp. 1-50.

Keller, J., and Staudt, R. (2005). Gas Adsorption Equilibria. USA: Springer Science Business Media.

Luengo, C., Brigante, M., Antelo, J and Avena, M (2006). Kinetics of phosphate adsorption on goethite: comparing batch adsorption and ATR-IR measurements. J Colloid Interface Sci 300: 511–518

Maluf, H. J. G. M., Silva, C. A., Curi, N., Norton, L. D and Rosa, S. D (2018). Adsorption and availability of phosphorus in response to humic acid rates in soils limed with $CaCO_3$ or $MgCO_3$. 42(1):7-20.

Mihoub, A., Bouhoun, M. D., and Saker, M. L. (2016). Phosphorus Adsorption Isotherm: A Key Aspect for Effective Use and Environmentally Friendly Management of Phosphorus Fertilizers in Calcareous Soils, Communications in Soil Science and Plant Analysis, 47:16, 1920-1929.

Njoyim, E. B. T., Mvondo-Ze, A. D., Alakeh, M. N and Onana, A. A (2016). Phosphorus

adsorption isotherms in relation to soil characteristics of some selected volcanic affected soil of foumbot in the west region of Cameroon. International journal of soil science., 11:19-28.

Oelkers, E. H and Valsami-Jones, E (2008). Phosphate mineral reactivity and global sustainability. Elements 4: 83–87.

Pierzynski, G. M., McDowell, R. W and Sims, J. T (2005). Chemistry, cycling, and potential moment of inorganic phosphorus in soils. In JT Sims, AN Sharpley, eds, Phosphorus: Agriculture and the Environment. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Inc., Madison, WI, pp 53–86.

Shen, J., Yuan, L., Zhang, J., Li, H., Bai, Z., Chen, X., Zhang, W., Zhang, F. (2011). Phosphorus Dynamics: From Soil to Plant. 156(3): 997–1005.

Sato, S and Comerford, N.B (2005). Influence of soil pH on inorganic phosphorus sorption and desorption in a humid brazilian Ultisol. 29:685-694.

Schoonheydt, R. and Johnston, C.T (2011). The surface properties of clay minerals. EMU Notes in Mineralogy, 11: 337–373

Surchi, K. M. S. (2011). Agricultural Wastes as Low Cost Adsorbents for Pb Removal: Kinetics, Equilibrium and Thermodynamics. International Journal of Chemistry, 3(3), 103-112. http://dx.doi.org/10.5539/ijc.v3n3p103

Tamungang, N. E. B., Mvondo-Zé, A. D., Alakeh, M. N., and Adalbert, O. A. (Phosphorus Adsorption Isotherms in Relation to Soil Characteristics of Some Selected Volcanic Affected Soils of Foumbot in the West Region of Cameroon. International Journal of Soil Science, 11: 19-28.

Tan, I. A. W., Ahmad, A. L., & Hameed, B. H. (2008). Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. Desalination, 225, 13-28. http://dx.doi.org/10.1016/j.desal.2007.07.005

Tening, A.S., Foba-Tendo, J.N., Yakum-Ntaw S.Y and Tchuenteu, F. (2013). Phosphorus fixing capacity of a volcanic soil on the slope of mount Cameroon. Agric. Biol. J. North Am., 4: 166-174.

Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R and Polasky, S. (2002). Agricultural sustainability and intensive production practices. Nature. 418, 671-677.

Thajeel, A. S (2013). Isotherm, Kinetic and Thermodynamic of Adsorption of Heavy Metal Ions onto Local Activated Carbon. Journal of Aquatic Science and Technology. 1:53-77.

Shen, J., Yuan, L., Zhang, J., Li, H., Bai, Z., Chen, X., Zhang, W and Zhang, F (2011). Phosphorus Dynamics: From Soil to Plant. American Society of Plant Biologists, Plant Physiology, Vol. 156, pp. 997–1005.

Turner, B. L., Richardson, A. E. and Mullaney, E. J (2007). Inositol Phosphates: Linking Agriculture and the Environment. CAB International, Wallingford, UK, p 304.

Uddin, M.K (2017). A review on the adsorption of heavy metals by clay minerals, withspecial focus on the past decade. Journal of chemical engineering, 308: 438-462.

Wang, Q., and Li, Y. (2010). Phosphorus adsorption and desorption behavior on sediments of different origins. J Soils Sediments, 10:1159–117.

Yaser, H. and Rahim, D.T. (2013). Comparison of phosphorus adsorption isotherms in soil and its relation to soil properties. Int. J. Agric.: Res. Rev., 3: 163-171.

Yang, X., Sun, Z., Wang, D and Forsling, W (2007). Surface acid–base properties and hydration/dehydration mechanisms of aluminum (hydr)oxides. Journal of Colloid and Interface Science 308 (2007) 395–404.