JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

ENVIRONMENTAL ENGINEERING PROGRAMME

PHOSPHORUS FIXING CAPACITY OF LATERITE SOIL BLENDED WITH SPENT COFFEE GROUND

BY

SEYOUM KETEMA

A THESIS SUBMITTED TO SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING, ENVIRONMENTAL ENGINEERING PROGRAMME, JIMMA INSTITUTE OF TECHNOLOGY, AND JIMMA UNIVERSITY FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING.

NOVEMBER, 2015

JIMMA, ETHIOPIA

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SENIOR ADVISOR: - Dr. FIKADU FUFA (PhD)
CO-ADVISOR: -   DR. DEJENE BEYANE (PhD)

NOVEMBER, 2015

JIMMA,ETHIOPIA

DELARATION

This thesis is my original work; it has not been presented in this and any other University. All sources of materials used in this thesis work have been duly acknowledged.

Name   Signature   Date

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This thesis has been submitted for examination with my approval as university Supervisor

Name   Signature   Date

1. _____ _____ /_____/_____/____

Chairman

2. _____ _____ /_____/_____/____

Principal advisor

3. _____ _____ /_____/_____/____

Co-advisor

4. _____ _____ /_____/_____/____

Internal Examiner

5. _____ _____ /_____/_____/____

External Examiner

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List of Abbreviations and Acronyms

P	Phosphorus
LS	laterite soil
SCG	Spent coffee ground
ATP	Adenosine tri phosphate
ADP	Adenosine di phosphate
^{o}C	degree centigrade
Kg	Kilogram
Mg	milligram
g	gram
L	liter
ml	millimeter
P_o	labile organic
P_i	labile inorganic
μm	micro molar
DNA	Deoxyribonucleic acid
RNA	Ribonucleic acid
CEC	Cation exchange capacity
$Ca_3 (PO_4)_2$	Tricalcium phosphate
$Al PO_4$	Aluminium phosphate
$FePO_4$	Ferric phosphate
OC	Organic carbon
Cmolc	centi mole change
cm	Centimeter

Abstract

Phosphorus fixation, which is responsible for low availability of P, is one of the major problems of crop growth in acidic soils such as LS. Therefore, the incubation study was conducted to determine the suitability of SCG as soil amender to reduce P fixing capacity of LS.

LS samples were collected from three different Karsa areas at depth of 0-15 cm using soil auger and SCG samples were collected from eight coffee houses at Jimma Town. Treatment soils containing 0, 20, 60 and 180 mg/L were prepared from KH_2PO_4. 25 ml portions of the treatment solutions were added to 2 g of LS samples and LS +SCG (2:0.25, 2:0.5, 2:0.75 and 2:1) in cups and were plugged respectively. The samples were incubated at room temperature and allowed to stand for 1, 3, 7, 14 and 28 days respectively. At the set days, the fixed P was determined using of Ascrobic Acid method. The amount of P recovered at different incubation periods increased with increasing a dose of SCG addition. The study revealed the percentage of organic carbon contents in both LS and SCG were as follows: LS (2.106%) < (47.95%). pH of LS (5.61) < pH of SCG (7.21) and available P of LS (41.91 mg/kg) < SCG (1745 mg/kg). The fixed decreased with added a dose of SCG throughout the incubation period in mixture of LS and SCG. The LS blended with SCG showed a less P fixing capacity between 60-66% as compared with LS which shows high P fixing capacity between 92-99%. Less than 63% of P fixation in the mixture of LS and SCG was decreased after one day of incubation.

Application of SCG is recommended for LS to increase soil fertility. Organic carbon and available P could therefore be responsible in minimizing of P fixation of LS.

Key words*: Phosphorus, fixing capacity, laterite soil, spent coffee ground*

Chapter One

Introduction

1.1 Background and Justification

Phosphorus is a fundamental macronutrient for plant growth and productivity, and lack of available P in soils can affect crop yields (Pay et al., 2001). P plays a great role to increase development of the root system mainly of the fibrous and lateral rootlets, a route through which the nutrients available for plants (Brady, 1984). Lack of available P in plants represents the second most significant soil fertility problem throughout the world (Sanchez and Salinas,1981). P is the most limiting element next to nitrogen in the Alfisols, Oxisols, and Ultisols of tropical and subtropical Africa, Asia, and South America (Sanchez, 1976). P shortage in such soils is often make worsen by a high affinity of the soils to fix (adsorb and/or precipitate) P which make less available it for crop (Owusu-Bennoah and Acuaye , 1989). Plants use orthophosphate ion as a nutrient like P from soil solution hence, plants and soil minerals compete each other for this form of P, especially in the highly weathered soils of the tropics, most of which characterized by large amounts of Fe oxides, Al oxides, or amorphous alumino-silicate clays. These soil minerals "fix" P strongly through a sorption process and making P almost unavailable for plant uptake (Morel et al., 1989). The P-fixing capacity of a soil is dependent on many factors, such as pH, $CaCO_3$ content, sesquioxides amount, and moisture and clay contents of the soil (Nad et al., 1975). Investigations of phosphate sorption characteristics of some Ghanaian revealed that the phosphate sorption maxima were high correlated with the soil properties in the order: Al_2O_3 clay content, free Fe_2O_3 and organic carbon (Pulschen, 1987). Study conducted on the investigation of phosphate fixing capacity of soils by the isotopic exchange techniques in north-east France reported that there was a significant correlation between amount of reported the significant correlation between amount of P fixed, pH, exchangeable cations, clay content and soluble phosphate (Soon, 1990). Sample depth also has effect on the P fixing of soils. Sampling depths of 10 and 15 cm frequently resulted in lower P fertilizer recommendation than those of 30-cm depth (Koenig et al., 2000).

The Ethiopian soils are also similar to the other agricultural soils of the tropics since it is located in tropic region in which its agricultural soils ,are generally low in available P and have reported that

70-75% of some Ethiopian agricultural soils are scarce in plant available P (Tekalign and Haque, 1987).

Due to the low available P, the fertility and productivity of the soil reduces to great extent hence causing food insecurity in regions where the soil is lack in P nutrient. Consequently, exploration of the mechanisms which is capable and practical to reduce the P fixing capacity of the soil is crucial for the increase of the crop yield of the farmers living in the highly leached soils like some of Ethiopia.

Therefore, the suitability of SCG as soil amending waste materials for the reduction P fixing capacity of LS was investigated at laboratory level.

1.2 Statement of the problem

Some representative major soil types in Ethiopia are low in P (Picolo and Huluka, 1985). Several authors have reported independently that 70-75% of some Ethiopian agricultural soils are deficient in P (Desta,1982). Soil acidity is a major serious problem to crop production particularly in the areas of the western, southern and central highlands of Ethiopia (Wassie and Shiferaw, 2009). low availability of P in low quantity under most soils of Ethiopia is due to the effects of P fixation by acidic cations, abundant loss of P by crop harvest and erosion and the inherent P deficiency of the soils by little or no P sourced fertilizers application (Asmar, 2014). Lupwayi and Huluka (1996) report that about 82% of Ethiopian highland soils are reported low in P deficient with Olsen extractable P concentration lower than 1 ppm. 70% of the Vertisols in the Ethiopian highlands are reported low in available P content, below 5 ppm (Hubble, 1984; Berhanu,1985). In addition, P sorption studies indicated that high sorption capacity of Vertisols and other soils in Ethiopia which is mainly controlled by content of Fe and Al oxides (Tekalign and Haque, 1987). The decrease in the available P in soil results in the decrease in the yield of crops. As a result the need for amending soil to increase the P availability is crucial to increase the productivity of the soil. Therefore, the aim of the study was undertaken to determine the effect of addition of SCG on phosphorus fixing capacity of LS.

1.3 Significance of the study

Blending LS with SCG would increase P available for plants; thereby increasing the productivity of the soil which in turn decreases the application of chemical fertilizer. The use of SCG can have double face importance, in that firstly it would prevent the environmental problems resulted due to the pilling of the waste from coffee processing; and secondly it could reduce the expenditure on chemical fertilizer.

1.4 Objectives of the study

1.4.1 General objective

The purpose of the study was to determine the suitability of SCG as soil amender to reduce P fixing capacity of LS.

1.4.2 Specific objectives

- To characterize LS +SCG;
- To determine the effect of pH and concentration of P on the p- fixing capacity of mixture (SCG+LS);
- To investigate the P-fixing capacity of blend of SCG and LS;

Chapter Two

Literature review

2.1. Importance of phosphorus

Phosphorus (P) is an essential element classified as macronutrient for the continuity and survival of living creation. Importance of it is listed next to nitrogen. Metabolism of micro to mega living things owes to existence of P. (Taiz and Zeiger, 1998), predicted that P is the constituent and parcel of ATP and ADP molecules, component of phospholipids and nucleic acid, to construct cellular membranes and make available compounds for photosynthesis in plants and respiration in animals. (Gutam and Tumar, 1997) also found that P plays a great role in many of the plant physiological processes like photosynthesis, utilization of sugar and starch and transfer of energy. It is also a part of energy generating process of phosphorylation. Function of P in energy storage and transfer is more important. In addition to this vital metabolic function, P is a significant structural constituent of a wide variety of biochemicals, including nucleic acids, which are the building blocks of genes and chromosomes and the essence of heredity. It is the component of cell nucleus and is indispensable for cell division and formation of meristematic tissues (Tisdale et al., 1993). It is also required for signal transduction, macro-molecular biosynthesis and respiration. Lacking adequate P supply result into loss of crop yield. Therefore, direct availability of P determines plant growth (Hinsinger, 2001). Plants need sufficient P from the very early stage of growth for optimum crop production (Grant et al., 2001).

2.2. Soil Phosphorus

Phosphate fertilizer is frequently applied to guarantee that sufficient P is available to optimize crop yield and maturity. Total soil P typically ranges from 100 to 2000 mg P/kg soil representing approximately 350 to 7000 kg P/ha in the surface 25 cm of the soil, although only a small portion of this P is immediately available for crop uptake (Morel, 2002). Soluble P compounds when added to the soil it react rapidly with various soil components, and are quickly converted to slowly available forms. The reaction between orthophosphate and soil is complex and generally ranges from true adsorption to the precipitation without clear separation between the two mechanisms (Mott, 1970). P fixation is a severe problem in alkaline and calcareous soils that

consequently establish low P concentration in soil solution (Sharif et al., 2000). The soils could adsorb large quantity of P for rapid and firm adsorption from solution and the adsorbed P was difficult to release from soil (Huang, 1998). The dynamics of P is managed by many soil properties in calcareous soils which strongly retain P and accordingly maintain low P concentration in soil solution (Bertrand et al., 1999). The degree of P sorption was comparatively higher in fertilized soil and highly available which in turn decreased with increasing rate of fertilizer P in both manured and non-manured soils (Reddy et al., 1999). Soils have propensity to retain equilibrium between solution P and adsorbed P. Only inorganic P (Pi) fraction of soil solution is used for plants which is the minimum fraction of total P available in soil. The P concentration of soil solution ranges from 0.1 to 1.0 mg/L (Yagodin, 1984). P utilized by plants in form of solution P is replenished by P from labile inorganic P (P_i) minerals and by bio-chemical mineralization of labile organic P (P_o). The total of P accessible to plant is determined by i) the pool size of labile P_i, ii) the transformation rates between labile and slowly reacting Pi and iii) the cycling rate of mineralizable Po (Tiessen, 1991) .

Nisar et al. (1985) used water soluble P and Mehlich-1 extractable-P as indicators of the potential for P to be released from manure impacted soil. The efficient utilization of nutrients with minimum nutrient losses is the main purpose of sustainable agriculture. This is especially true for P, since it is a limited resource (Oenema et al., 2000). Plants absorb P for their growth from soil solution. It disturbs equilibrium between soil solution, P concentration and the labile pool at the solid soil phase which leads to release of P into the soil solution. In non labile fraction, about 90% of total P is present as insoluble or fixed forms, including 7 primary phosphate minerals, humus P, insoluble phosphate of Ca, Fe and Al and P fixed by hydrous oxides and silicate minerals P availability in soils is greatly hindered by binding to oxides of Fe and Al. On the other hand, P moves through soil profiles only by diffusion not with flow of water. Therefore, just about 1 % of Po pool per year is mineralized, supplying Pi for plant uptake (Tiessen, 1991); a very limited system for the recycling of small amounts of P in soil gets developed.

P is comparatively less mobile and least available major plant nutrient in soil. It moves very little from the site of its application. The results are in complex situation as compared with those for other nutrients (Archer, 1988). Due to the reason the efficiency of utilization of fertilizer P by plant is very low and its recovery ranges from 15-25% (Nisar et al., 1985). It is therefore

frequently a major or even the prime limiting factor for plant growth. Natural equilibrium between solid and solution phases and soil constituents controls P availability in soils. In spite of increased total P contents of fertilized soils, majority of soils respond the application of P (Tandon, 1987). In fact, soil P reserves are sufficient but their availability to plants is quite insufficient. A huge land area (5.7billion hectares worldwide), contain too little available P to sustain optimal crop production (Batjes, 1997; Gaume, 2000). High reactivity of phosphate ions against various soil constituents and the retention capacity of such constituents results into poor mobility of soil Pi. A considerable part of applied P also binds with Ca, Al and Fe, depending upon the soil pH (Singh, 2001). Thus, only a minor portion of solution P in soil is present as P ions in the soil. Although P ions can be accumulated in larger concentrations in highly fertilized soils, however, it remains in micro molar range of 0.1 and10µM which is inadequate for optimal plant growth (Ozanne, 1980; Mengel and Kirkby, 1980, Raghothama, 1999; Frossard et al., 2000). Average range of P concentration in plough layer is 500-14000 kg P_2O_5 /ha and 0.2-7.0 g kg soil while soil solution has 0.07-0.5 mg P/L (Hedley et al., 1995). Deficiency of P is the common feature of calcareous/alkaline soils of Mediterranean region and highly weathered soils of tropics and subtropics (Hinsinger, 2001).

2.3. Soil phosphorus chemistry

2.3.1. Soil organic phosphorus

The levels of p organic in soils vary widely, ranging from zero to over 0.2 percent soil mass. The organic fraction generally constitutes 20 to 80 percent of the total P in surface soil horizons (Brandy and Weil, 2002). McLaughlin et al. (1990) Postulated that organic P in soil generally accounts for around 50 percent of total soil p and up to 80 percent of the total P for pastures soil. In Australian soils, inositol P has been shown to constitute up to 29 percent of the total organic P (Williams and Anderson, 1968).
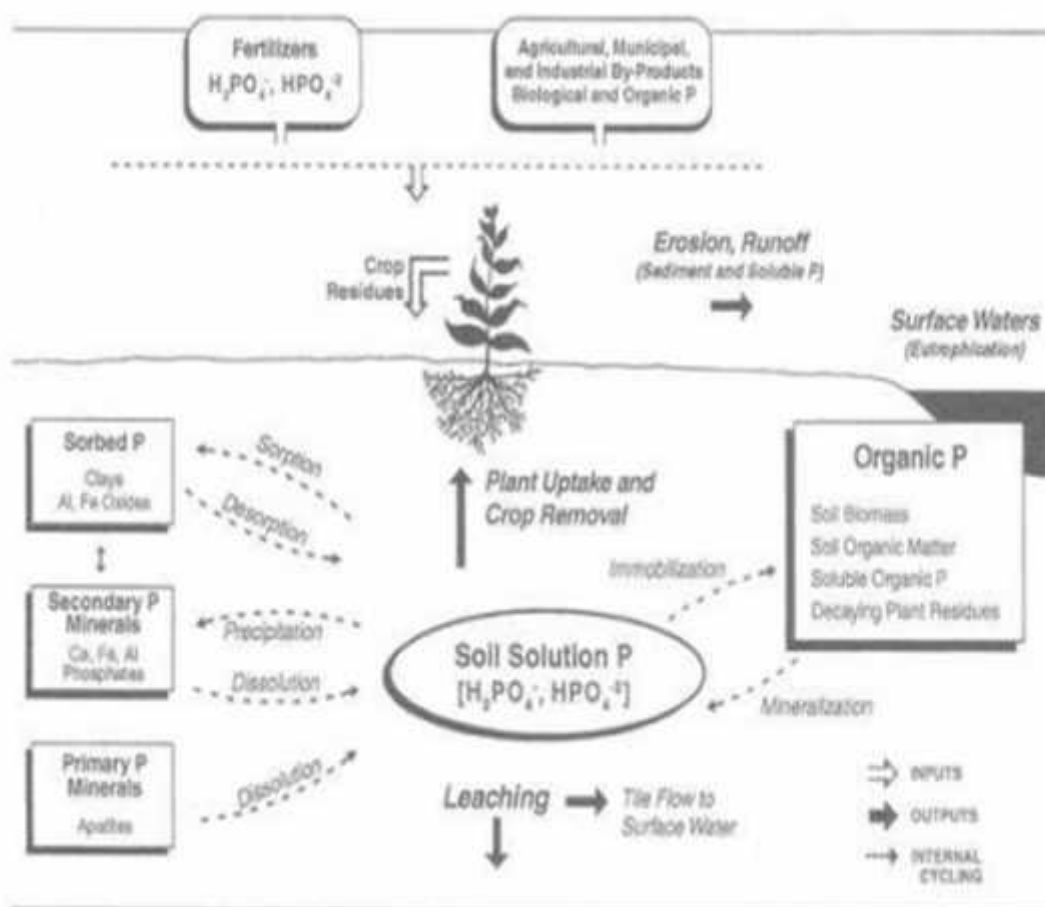
Figure 2. 1 Soil plant phosphorus cycle (Sims and Sharply, 2005)

The diagram shows that P fertilizer added to soils can be converted to ionic forms available to plants. Ionic P becomes unavailable to the plant after adsorption reactions with clay, Al, and Fe oxides, and Ca, Fe and Al phosphates. Some available P becomes unavailable by immobilization with the soil biomass. Available P is taken up by plants is lost from the soil by crop removal (Sims and Sharply, 2005).

Inositol phosphates

The most abundant organic P compounds yet found in soils are the stable group of inositol hexaphosphates, six membered carbon rings with a phosphate group on each carbon.
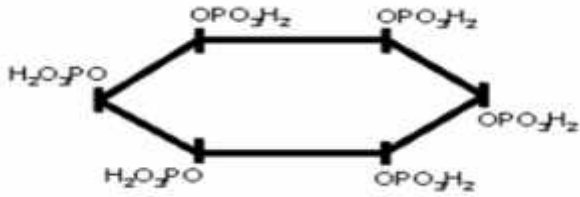
Structural confi guration of inositol hexametaphosphate (Hesse, 1971).

All the phosphate groups are linked to the inositol as esters and have two replaceable hydrogen atoms; in soil these are most probably replaced by iron, Al, Zn, Ca and Mg (Cald well and Black, 1958).

Inosital are homocyclic sugar like compound$[C_6H_6(OH)_6]$, which can form series of phosphate esters ranging from monophosphates to hexaphosphate.phytic acid (myo-inositol hexaphosphoric acid) is the most common ester of this group and forms phytates in soils. The inositol phosphates are released from organic materials in soil at much slower rate than many other esters, but they are quickly stabilsed and can accumulate in some soil so that they account for more than 50 percent of the organic P and about 25 percent of the total P (Tisdale et al., 1985).

Inositol hexaphosphate forms a number of very insoluble salts through reactions with iron and aluminium under acid conditions and with calcium in alkaline solutions. It also forms strong complexes with proteins and with some metal ions. In these forms, inositol hexaphosphate is more resistant to enzymatic attack than are the more soluble ester salts.

Clay minerals such as montmorillonite and finely divided sesuioxides will strongly adsorb inositol hexaphosphate. Other myo- inositol phosphates are adsorbed, with the degree of adsorption decreasing with declining numbers of phosphate groups.

Nucleic acids

Both deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) occur in all living organisms. Each consists of a chain of sugar units, either ribose of deoxyribose, joined by phosphate ester bridges. A nitrogenous base derived from either urine or pyrimidine is attached to each sugar molecule. It is assumed that nucleic acids are released into soil much more rapidly than inositol phosphate and that they are broken down quickly. It is difficult to isolate pure nucleic acid from soils; its measurement has often been based on the quantities of nucleotides or purine and pyrimidine derivates released by hydrolysis of soil organic matter fractions. More recently, modified techniques for separation of

DNA from soil have been investigated, enabling the microbial biodiversity of soil to be analysed (Stackebrandt, 2003).

2.4. Inorganic phosphorus compounds

There are two groups of inorganic compounds in the soil. These are Ca compounds and Fe and Al compounds. Ca compounds are found in alkaline soil where they are more stable and insoluble than Fe and Al compounds. Ca compounds become more soluble as soil pH decreases, tending to dissolve in acid soils. Of the common calcium phosphates, the apatite minerals are the least soluble and therefore the least available source of p. Some apatites such as fluorapatites $(Ca_5(PO_4)_3F)$ are so stable that they persist even in acid soils. P from the similar monocalcium phosphate $(CaH_2PO_4)2.H_2O))$, as found as super phosphate, and to a lesser extent dicalcium phosphates $(CaHPO_4).2H_2O))$, is available for plant uptake (Brandy et al., 2002). Typical iron and calcium hydroxyl phosphate minerals are strengite $(FePO_4.2H_2O)$ and variscite $AlPO_4.2H_2O)$, which are insoluble in strongly acid soils become more soluble as soil pH rises (Brandy and Weil, 2002).

2.5. Phosphorus in the soil solution

The solubility of the inorganic forms of P is more serious problem for p nutrition plants than for any other macronutrient. P is unavailable in high and low pH ranges of soil solution. The most favorable pH for availability is near neutral to slightly acid. P is adsorbed by plants largely as the primary, secondary and tertiary orthophosphate ions ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}), which are present in the soil solution and the amount of each form depends on the pH of the soil solution (Troeh and Thompson, 1993). Most of the P absorbed by plants is in the monovalent orthophosphate form, $H_2PO_4^-$ which is predominant at pH values below 7.2 and is typical of most agricultural soils. The free interconvertible HPO_4^{2-} a form which is more dominant above pH 7.2, may be some plants. Another phosphate ion (tertiary orthophosphate PO_4^{3-}) occurs at pH values too high for it to be significant in plant nutrition. Even at a pH of 12 the HPO_4^{2-}, concentration is relatively greater than that of PO_4^{3-} (Kardos, 1967).
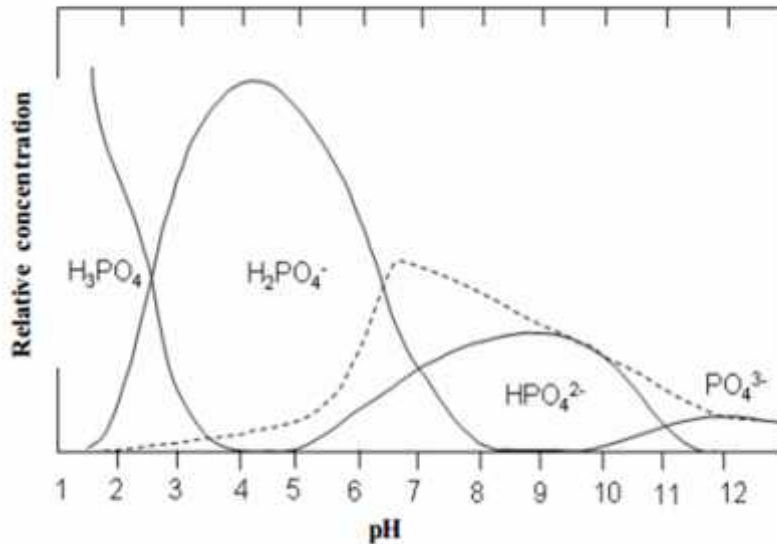
Figure 2.2 Proportions ions of phosphate ions in solution at different pH levels in a CaH_3PO_4 System.

The dashed lines shows the upper limit of available P in solution imposed by the solubility of calcium phosphates above pH 6.5 or iron and aluminum phosphate below pH 6.5 (Troeh and Thompson, 1993).

2.6. The phosphorus status of soil

For agriculture, the management of available P is second only in importance to the management of available nitrogen for the production of healthy plants and profitable yields. Inadequate supplies of soil P restrict plant growth and reduce the benefits from available nitrogen. Different figures for organic, inorganic and total P in soil have been reported. (Hemwall, 1957) reported that the measured organic P pool in soils fall between 20kg/ha and 4000kg/ha which is highly variable availability. Lindsay et al. (1977) stated that P in Australian soils usually fall between 200 mg/kg and 5000 mg/kg with an average content of about 500mg/kg. The total P content has been stated to be between 100 and 2500kg/ha with an average value of about 1000kg/ha in the surface 20cm of soil (Tisdale et al., 1985). In another the total P content in average soils has been illustrated as about 500mg/kg but only about 0.1 percent of the total P is available to plants (Scheffer and Schachtsabel, 1992). Apart from nitrogen, the level of P in soils is more than that of any other single nutrient which governs soil fertility (Norrish and Rosser, 1983). Even though some soil

profiles have a higher P pool in the surface soil as a result of adding fertilizer, immobile element in the landscape and hence the fertility of soil is inherited from its parent material. The other major soil nutrients such as N, S, Mg, Ca and K are more mobile and the parent material is not such a controlling factor. Lindsay et al. (1977) suggested that the P required by wheat crop is only a small fraction of the total P in the top 15cm of the soil. Available P is dynamic and many soils cannot provide P at an enough rate for plant growth and the presence of enormous amounts of unavailable forms of P is formed. There is no easy relationship between the amount of P available and the total P content. Only about 1 percent of P applied as fertilizer to the soil is used by plants in the subsequent cropping season and the remaining 8 percent forms different insoluble complexes in the soil. The added fertilizer to the soil to increase the P content of the surface soil, however, under normal agricultural practice the annual increase in total P is slight (Norrish and Rosser, 1983).

2.7. Phosphorus fixation in soil

The process of soluble phosphate anions being bound with soil constituents and form it become insoluble and an unavailable to plants is known as fixation. Numerous mechanisms of P fixation have been reported. These are precipitation- dissolution reactions, adsorption-reactions, and immobilization mineralization reactions. In the most recent quarter century, the researcher has been found that relatively fast reactions by which P is either adsorbed by or desorbed from soil solids with charged surfaces (Tisdale et al., 1985). Later on researchers tend to conclude that adsorption-desorption reactions on soil constituents has a greater significance than precipitation- dissolution reactions of P minerals. Adsorption is defined as the net accumulation of matter at the interface between a solid phase and aqueous solution (Sposito, 1989).

2.8. Phosphorus fixation in acid soil

Fe and Al oxides and hydroxides are the substances that have been identified in P fixation in acid soils. (Toth, 1937) demonstrated that the removal of the free iron oxide content of soil colloids reduces the degree of P fixation showing that these compounds are partially accountable for P fixation. It has also been postulated and demonstrated that iron and aluminum sesquioxides play a significant role in P fixation Struthers et al. (1950). Amorphous and poorly crystalline Fe and Al minerals are frequently involved in P adsorption process in soils (Pant et al., 2002). Solubility of

Phosphate and its reactions are influenced by predominantly the dissolution- precipitation activities of amorphous Al, Fe and crystalline iron oxides (Zhang et al., 2002). The fixation reactions can occur between phosphate and Fe or Al ions and iron and hydroxides aluminum or between phosphate and silicate minerals. In addition, silicate clays demonstrated that when crystalline products can be detected they are usually either simple Al or Fe phosphates related to variscite, or alkali Al/F phosphates. Relate to taranakite (Haseman et al., 1950; Kittrick and Jackson, 1955; Lindsay and Stephenson, 1959). The free Fe, sesquioxide clays and Al react rapidly with phosphate, forming a series of difficultly soluble hydroxyphosphates such as monodentate complex. Hydrous oxides of aluminum and iron were mostly responsible for the fixation of phosphate in soils
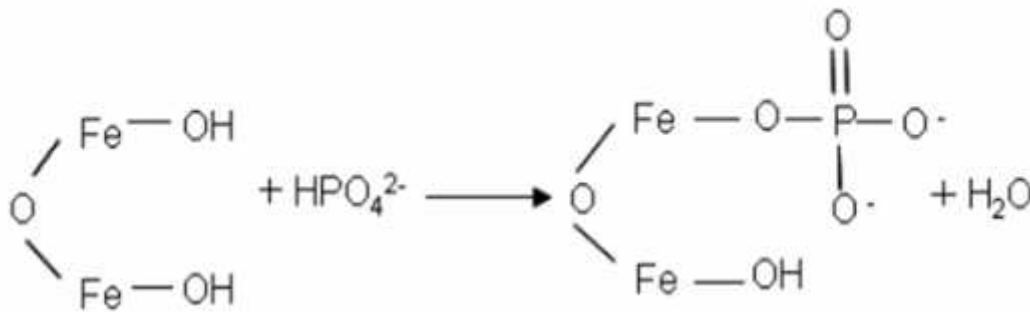
Monodentate complex (liable)

Figure 2.3 Structural arrangement of phosphate fixation with iron (monodentate complex) in acidic soil conditions (Tan, 1993).
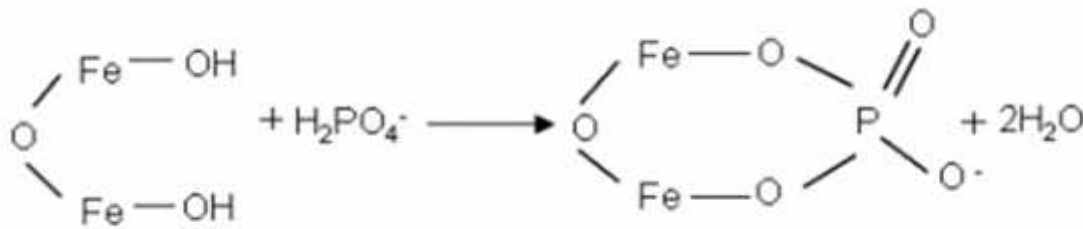
Bidentate complex (irreversible)

Figure 2.4 Structural configuration of phosphate fixation with iron (bidentate complex) in acidic soil conditions (Tan, 1993).

Phosphate retention can be occurring mainly in acidic soil conditions in contrast phosphate fixation by hydrous oxide clays over relatively wider pH range. The products formed by both retention and fixation reactions are not pure Al or pure Fe phosphate. Solubility criteria imply that the immediate reaction of applied phosphate products in acid soils is moderately soluble but depending on ageing, the intermediate reaction products are slowly changed to variscite, which may coexist with gibbsite as a stable solid phase (Lindsay et al., 1959). A similar reaction happens in the case of iron. varscite $AlPO_4.2H_2O$) is the ultimate end product formed between Al hydroxides and phosphates where strengite $FePO_4.2H_2O$) formed between Fe and phosphate; these two products are the least soluble (or most stable) compounds at acid pH range. A series of intergrades between variscite and strengite is usually present in soils and is called the variscite- strengite isomorphours (Lindsay et al.,1959)**.** Moreover, the formation of Fe and Al phosphate ($FePO_4$) and $AlPO_4$ is mostly unlikely to responsible for much P fixation except where pH is less than 4 (Hemwall, 1957). According to potentiometric titration curves for Fe and Al chlorides in the presence of varying amounts of phosphate indicated that in the pH range of acidic soils, the compounds formed are $Fe(OH_2)_3(OH)2H_2PO_4$ or $Al(OH_2)_3(OH)2H_2PO_4$ rather than $FePO_4$ or AlO_4 (Swenson et al.,1949).

Silicate clays is another types of phosphate fixation which in acidic conditions with phosphate. Especially in the case of soil clay minerals exhibiting exposed hydroxyl groups, such as the kaolinitic groups, there is a strong affinity for phosphate ions. Phosphate ions react rapidly with octahedral aluminium by replacing the hydroxyl groups located on the surface plane of the mineral. Generally, clays (example kaolinite) with low SiO_2/R_2O_3 (sesquioxide) ratios have higher phosphate fixing capacity than clays (montmorinite) with high SiO_2/R_2O_3 (sesquioxide) ratios (Tisdale et al., 1985). Thus P fixation in acid soils is primarily due to the presence of Fe and Al compounds in the form of M $(H_2O)_3(OH)2H_2PO_4$. The Fe and Al containing soil minerals, including the clay minerals, are the source of the Fe and Al. The formation of these compounds is governed by the solubility product, the common ion, and salt effect principles. Under certain conditions, a precipitate is formed, whereas under other conditions the compounds adsorbed (Hemwall, 1957).

2.9. Phosphorus fixation by clay minerals

The availability of P in alkaline soils is determined principally by the solubility of the various Ca-phosphate compounds present and the reactions of P with clay minerals causing p fixation in soil have been studied. Al is one of the elements which associated with clay and it is responsible for this fixation (Hemwall, 1957). It was deduced that P fixation by clay minerals was clearly related with the sesquioxixe Al content of the clays not the intact aluminium silicate clay minerals (Coleman, 1944). The amount of P fixed in clay mineral was indicated to be proportional to the amount of free Al oxide on the clays; and that fixation occurs as long as due to Al availability in clay substance. Additional support for the hypothesis is that free aluminium oxides are necessary for clay minerals to fix P was provided by demonstration that montmorillonite will not fix P once all Fe and Al oxides are removed from the clay (Ellis and Troung, 1955). It was shown that the presence of fluoride or aluminium tricarboxlic acid, both strong complexing agents for aluminium, inhibits the fixation of P by montmorillonite (Hemwall, 1957). Moreover, the X- ray diffraction evidence showed that fixed P is not sorbed between the lamellae of the clay minerals and does not interfere with the swelling properties of the clay. An experimental procedure for developing a P retention characteristic of soil layers has been developed (Pant et al., 2002). The P adsorption maxima were positively correlated with oxalate aluminium and citrate dithionite bi carbonate extractable aluminium under conditions, but there was no significant correlation with either oxalate extractable iron or citrate dithionite bi carbonate extractable iron. The X- ray diffraction patterns indicated that smectite was the dominant mineral in the clay size fraction. It is likely that the permanent negative charge of smectite limits its concentration to P adsorption.

2.10. Phosphorus fixation in alkaline soil

Soil phosphate fixation is not limited to acidic soil conditions only. But also it occurs in alkaline soil. P fixation in alkaline calceeous soil is usually attributed to the formation of insoluble phosphate compounds of Ca. The compounds of Fe and Al were discussed in relation to fixation in acid soils are responsible for some fixation in soils of higher pH (Hemwall, 1957).

However, alkaline soils contain high amounts of soluble and exchangeable Ca^{2+} and, frequently, $CaCO_3$ (Tan, 1993; Brandy and Weil, 2002). In these alkaline soil conditions, phosphate is

reported to react with both the ionic and the carbon in the form Ca the reactions as illustrated in Equations (1) and (2).

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \qquad (1)$$

(Insoluble)

$$Ca(H_2PO_4)2.H_2O + 2CaCO_3 \rightarrow Ca_3(PO_4)_2 + 2CO_2 + 3H_2O \uparrow \qquad (2)$$
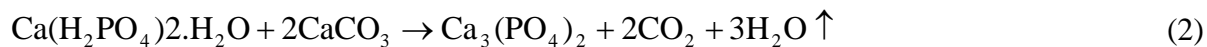
Monocalcium   (insoluble)

Phosphate (soluble)

Hydroxyapatite $[Ca_5(PO_4)_3OH]$, oxyapatite   carbonated apatite $(Ca(PO_4)_3CO_3)$ and   Ca-fluoroapatite $(Ca_5(PO_4)_3F)$ are other types of Ca phosphate which exist in the form of insoluble and formed between calcium and phosphate in alkaline soil condition (Brandy et al., 2002). The role of clay minerals in P fixation in alkaline soil was shown that P can be fixed by the $Al(OH)^{2+}$ in the clay fraction of alkaline soils (Wild, 1953). This category of fixation is more serious problem in a rid region soils; however, it can also become a significant in the acid tropical soils when the soil needs high applications of lime. In such conditions, applications of P fertilizers generally give low plant growth responses.

2.11. Factors affecting phosphorus fixation in soil

Mechanisms of P fixation reactions and some preliminary factors influencing P fixation are apparent. Because of the importance of retention and fixation in modifying the effectiveness of applied fertilizer P, these factors, and the extent to which they influence fixation, need further consideration. These factors are: (1) the nature and amount of soil components (2) pH, (3) other ions and (4) saturation of the adsorption

2.11.1. Nature and amount of soil components

Adsorption-desorption reactions are affected by the types of surfaces contacted by P in the soil solution.

Hydrous metal oxides of iron and aluminium: these substances, especially the hydrous ferric oxides gel that have the capacity to adsorb very large amounts of P. Due to the presence of these substances in all soils; they are most abundant in well weathered soils. Al and Fe oxides and their

hydrous oxides can be occur in the form of discrete particles in soils or in a coatings of or associated with other soil particles. It can also exist in the form of amorphous aluminium hydroxyl compounds between the layers of expandable aluminium silicates in clay minerals.

Generally, it is accepted that soils with significant contents of Fe and Al oxide, the less crystalline the oxides are, the larger their P fixation capacity because of their greater surface areas. However, crystalline hydrous metal oxides are usually capable of retaining more P than clay layer silicates.

Type of clay: The sorption of P is more in the oxides of Fe and Al and which retained to a greater extent by 1:1than 2:1clays.The layers of the 1:1 type minerals are made up of one tetrahedral (silica) sheet and one octahedral (alumina) sheet, while 2:1 type minerals are characterized by an octahedral sheet (Brandy and Weil, 2002).

Soil high in kaolinite clays, such as those found in areas of high rain fall and high temperature can fix or retain larger quantities of added P than those containing the 2:1.soils containing large amounts of clay will fix more P than those containing small amounts. The more the surface area exposed with a given type of clay, the greater amount of fixation take place. Clays such as kaolinite with a low SiO_2/R_2O_3 ratio (R represents the elements aluminium or iron in sesquioxide) can fix larger quantities of P than clays with a high ratio. Kaolinite with a 1:1 silica/alumina lattice has larger number of exposed hydroxyl groups in the gibbsite layer that can be exchanged for P.

Clay content: soils containing large quantities of clay can fix more P than those comprising smaller amounts clays and more siliceous and silt. To some extent, the greater surface area exposed in high clay soils, the greater the tendency to retain P.

Amorphous colloids: in young soils texture is often meaningless due to the presence of high amounts of X-ray amorphous colloids. P retention in these soils closely related to the content of X-ray amorphous colloids and with surface area (Tisdale et al.,1985).

Calcium carbonate: a minor portion of the P sorption capacity of soils is originated from calcium carbonate. Much of the adsorption attributed to it, however, may actually be due to hydrous ferrioxide impurities. The activity of P will be lower in those soils that have a high Ca^{2+} activity, a large amount of highly reactive calcium saturated clay (Tisdale et al., 1985).

2.11.2. Effects of pH on predominantly insoluble phosphorus change

Soil pH has profound influence on the amount of soluble P fixed and the manner which it becomes fixed. Adsorption of P by Fe and Al oxides declines with increasing pH. Raising the pH of clays

above 4 can increase p adsorption because the increase in hydration of Al^{3+}. Raising pH may, however, reduce p adsorption where interlayer hydroxyl aluminium polymers exist, as in many types of vermiculite.

Phosphorus availability most soils are at a maximum in the pH range 6.0 to 6.5. At lower pH values, retention results largely from the reaction with iron and aluminium and their hydrous oxide. Above pH 7.0 the ions of calcium and magnesium, as well as the presence of carbonates of these metals in the soil, cause precipitation of the added P, and its availability again decreases.
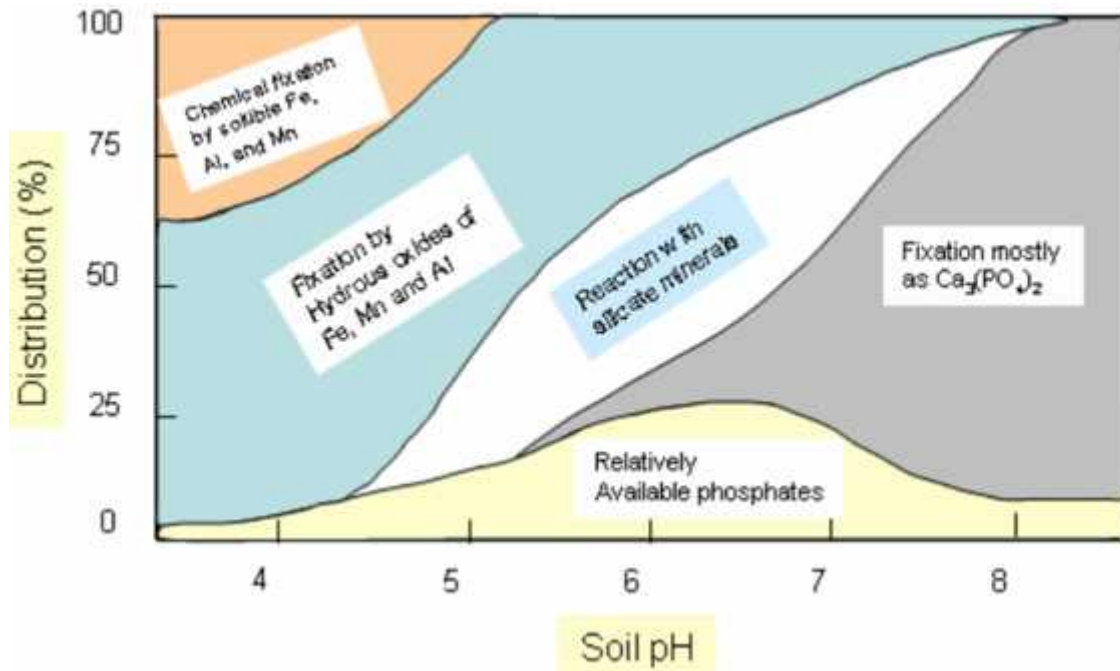
Figure 2.5 Phosphate availability and fixations related to soil pH (Brandy and Weil, 2002).

Average conditions are postulated it should not be presumed that any particular soil would have exactly this distribution. The actual proportion of the phosphorus remaining in an available from will depend upon contact with the soil, time for reaction and other factors. Some of the added phosphorus may be changed to organic form in which it temporarily unavailable (Brandy and Weil, 2002).

Ionic effects

Cationic effects: adsorption of P by soil is influenced by the species and concentration of cations in the system. Divalent cations enhance P adsorption relative to monovalent cations. Example; clays saturated with Ca^{2+} can retain greater amounts of P than those saturated with sodium or other monovalent ions. Current explanations for this effect of Ca^{2+} involve making positively charges

edges sites of crystalline clay minerals more accessible to the P anions (Tisdale et al., 1985). This action of Ca^{2+} is possible at pH values lightly less than 6.5, but in soil more basic than this, dicalcium phosphate and other more basic calcium or magnesium phosphate would probably be directly precipitated from solution. Sheng et al. (2006) reported that higher pH value causes the surface to carry more negative Charges and thus would more significantly repulse the negatively charged species in solution.

Anionic effects: Both inorganic and organic anions can complete in varying degrees with P adsorption sites, resulting in some cases in a decrease in the adsorption of added P or desorption of retained of P. Weakly held organic anions, such as nitrate and chloride are of little consequence, whereas specifically adsorbed anions and acidic such as hydroxyl, sulfate and molybde, and silicic acid can be competitive. The strength of bonding of the anion with the adsorption surface determines the competitive ability of that anion. Phosphate is capable of forming stronger bond at the surface than is sulphate (Tisdale et al., 1985).

Saturation of the adsorption complex: The amounts of P adsorbed by soil are dependent on the number of available sites for reaction with the added P. similarly desorption of P is strongly influenced by the extent of saturation of the desorption complex. Ease of adsorption of is greater at higher saturations because P is sheld less tightly with increasing surface coverage. These correspond to higher action steady state, requiring less energy to cause dissociation (Kennedy, 2001). There is a pronounced relationship between the amount of the fixation of added fertilizer P and the R_2O/P_2O_5 ratio the soil, where R represents the Fe and Al content of soil. The R_2O/P_2O_5 R ratio is a measure of amount of P present in relation to the Fe and Al oxide content of the soil. A high ratio indicates a small amount of P present or a low P saturation value. Under such conditions larger amounts of added P can be fixed when the ratio is small.

Organic matter: it has been demonstrated that organic P compounds are mobile in soils to a greater depth than inorganic P. A range of organic P compounds moved to six times deeper into a clay loam than did inorganic P (Tisdale et al., 1985). It is well established that certain inorganic ions arising from the decomposition of organic matter can form stable complexes with iron and aluminium by chelating them, thus preventing their reaction with P. The anions that are most effective in replacing phosphate are citrate, oxalate, tartrate, malate and malonate some of which may be produced as degradation products during organic matter decay. It also found that allophonic surfaces adsorb P resulting in the formation of organic matter P associations, and also the humus P

complexes make up the major portion of total P in allophonic (Borie et al., 1983; Banik et al., 2006). In addition, the addition of organic manure markedly increased the availability of P in the soil. Organic matter mainly could made from fulvic acids material which form loosely bound compounds thus P could be easily released with time (Le Mare, 1991) Organic molecules released on decomposition of organic matter form organic molecules is block the active sites a place where Fe and Al complexes are attached hence fixation of phosphorus in soil is reduced (Juo and Fox, 1977; Brouwere, 2003; Ghosal et al., 2011). Erich et al. (2002) elucidate that the deprotonation of carboxylate group (COOH), phenolic and alcoholic hydroxyls (OH) reduce soil acidity. Halvin et al. (1999) report that P fixation tends to be more pronounced and ease of P release tends to be lowest in soils with higher clay content.

2.12. Adsorption-desorption behaviour of phosphorus in soil

2.12.1. Adsorption of P by different soils and under equilibrium solutions

The buffering capacity of P has been defined as the relationship between change in adsorbed P (P) and the activity of H_2PO_4 (Beckett et al., 1964). This relationship is similar to an adsorption isotherm. It differs that the scale of the vertical axis is related to the initial P status rather than to zero. This relationship is usually found to be curved. The effects of soil buffering capacity on P desorption have been examined by different methods.

The effect of the soil P buffering on the uptake of P by soft brome (Bromus mollis) grown in 42 different surface soils has been examined (Barrow, 1978). The premaining in the soil was extracted by sodium bicarbonate. The experiment was conducted on soft brome grass in a pot trial where grass was grown for 183 days in a glass house in 1.6 kg of 42 different surface soils. The tops were clipped on five occasions. A strong relationship was found in P uptake between extractable P and P buffering capacity. For given value of extractable P, uptake was greatest on soils of lowest P buffering capacity. It was concluded that the bicarbonate extraction procedure may over estimate the availability of P in soils of high P buffering capacity. This probably occurs because at equal values of bicarbonate soluble P, a soil of low P buffering capacity has a higher solution concentration of phosphate. As 0.01 M $CaCl_2$ is a weak extractant (Brookes et al., 1984), it could

give a useful variation among the treatments in sol with high P buffering capacity. In a study of this kind the use of 0.01 M $CaCl_2$ solution as an extractant could reveal more useful information.

The affinity for P adsorption decreases as the amount of adsorption increases (Barrow, 1978). This effect is inherent in the process of P adsorption and occurs because specific adsorption of anions increases the negative charge on the adsorbing surface. It was also found that the acidic ammonium fluoride extractant of Bray and Kurty was the most sensitive to P buffering in this respect (Holford, 1988), while the alkaline sodium bicarbonate test of Colwell least sensitive to P buffering (Holford, 1988). It was reported that $NaHCO_3$ extractable P was much more closely correlated with total P uptake from mixed groups of soils than the quantity of labile P, but less correlated in the uniform group (Holford, 1988). Sodium bicarbonate is known to extract varying quantities of non labile P, by hydrolysis of iron and Al phosphates, especially from acidic and neutral soils (Holford, 1988).

2.13. Laterite Soil

The term laterite is derived from the Latin word later, meaning brick. It was first used in 1807 by Buchanan to describe a red iron-rich material found in the southern parts of India. Laterites are widely distributed throughout the world in the regions with high rainfall, but especially in the inter-tropical regions of Africa, Australia, India, South-East Asia and South America, where they generally occur just below the surface of grasslands or forest clearings. Laterite soils are one of important soils and are widespread in tropical areas and subtropical climates. They are the most highly weathered soils in the classification system. The significant features of the lateritie soils are their unique color, poor fertility, and high clay content and lower cation exchange capacity. In addition, lateritic soils possess a great amount of Fe and Al oxides (Shaw, 2001; Ko et al., 2006). Fe oxides, existing mainly in the amorphous and crystalline inorganic forms, are one of major components in many soil orders. Their extension indicates that conditions are favorable for their formation at some point in time in the history of the world, but not necessarily simultaneously in all regions (Maignien, 1966).

2.13.1 Composition and Properties of Lateritic Soils

The mineralogical and chemical compositions of laterites are dependent on their parent rocks (Tardy, 1997). Laterites consist mainly of quartz, zircon, and oxides of TiO_2, Fe, Al and MnO, which remain during the course of weathering.

Laterites vary in color, but are usually brightly colored. The shades most frequently encountered are pink, ochre, red and brown; however, some occurrences are mottled and streaked with violet, and others exhibit green marbling. A single sample may exhibit a whole range of colors merging more or less perceptibly into one another in a variety of patterns and forms. Laterites owe their color to iron oxides in various states of hydration and sometimes also to manganese (Maignien, 1966). Their mineralogy generally involves quartz, kaolinite, hematite, goethite and sometimes (Billong et al., 2009). Due to the weathering, the minerals and the oxides in the soil solution have a relatively low charge and the cation exchange capacity is very low. For example, oxisols and other soils of the tropics dominated by kaolinite have a CEC which is one third to one sixth that of other 2:1 clay dominated soils (15-30 cmolc/kg versus < 5 cmolc/kg).

The physical properties of LS vary according to the mineralogical composition and particle size distribution of the soil. The granulometry can vary from very fine to gravel according to its origin, thus influencing geotechnical properties such as plasticity and compressive strength. One of the main advantages of lateritic material is that it does not readily swell with water. This makes it an excellent packing material particularly when it is not too sandy (Maignien, 1966).

2.13.2. Chemical and Mineralogical Properties of LS

High content of the sequioxide of Fe and/or Al relative to the other component is the features of LS. These essential components mixed in variable proportions. Some laterite may contain more than 80% of Fe_2O_3 while other may contain up to 60% of alumina and only a few percent of Fe_2O_3.

One problem specific to soils rich in Fe, such as laterites, are that those negatively charged sights which are available to store nutrients are taken by Fe and sometimes Al and are therefore not available to store other nutrients (Duxbury et al., 1989; Wambeke, 1992).

2.14. Spent coffee ground

Spent coffee grounds obtained after the brewing process in cafeterias and restaurants, at home, or by the soluble coffee industry. Estimated worldwide annual production of SCG is around 6 million tons (Mussatto et al., 2011). In the last years, an increase of coffee beverages consumption has been observed all over the world. The preparation of this beverage generates high amounts of (SCG), which is usually mixed with common garbage (Tokimoto et al., 2005; Mussatto et al., 2011; Cruz et al., 2012). SCG could be used, for example, to produce fuel for industrial boilers due to its high calorific power of approximately 5,000 kcal/kg (Silva et al., 1998), as a substrate for cultivation of microorganisms Machado et al.(2012) and as raw material to produce fuel ethanol (Mussatto et al., 2012) or a distilled beverage with aroma of coffee (Sampaio et al., 2013).

As with other agricultural and food wastes, coffee solid residues have high volume but low value, which results in reduced global economic interest. Thus, generally, they are used either for energy production or disposed to landfill, causing major environmental issues. Several studies have been published on the last decade dealing with possible strategies to reduce their toxicity and enhance their commercial value, including animal feed, mushroom production, biodiesel, fuel pellets or activated carbons (Franca et al., 2009). The excessive use of organic fertilizers in agriculture is also an issue of global concern, due to the associated decrease in soil fertility, increase bulk density, soil and ground water pollution, and contamination of produced vegetables; all with direct consequences on human health (Kasongo et al., 2011). The preparation of coffee beverage generates high amounts of (SCG), which is usually mixed with common garbage (Mussatto et al., 2011; Cruz et al., 2012), causing major environmental issues. Therefore, finding strategies to valorise the utilization of this organic residue is of much interest. The chemical composition of SCG indicates several applications to this residue. For instance, the presence of nitrogen (about 1.2 – 2.3%), phosphorus (0.02 – 0.5%) and potassium (0.35%) contents Mussatto et al.(2011, Cruz et al.(2012) suggests its utilization on agriculture as fertilizer or as soil conditioner (Kondamudi et al., 2008).

SCG could be such an interesting approach: their rigid cellular structure can contribute to the recovery of soils structure, able to contribute a large amount of organic matter to the soil, which can increase soil water holding capacity as well as nutrient retention and aeration (Kasongo et al., 2011). Nutrient holding is key to prevent leaching of elements like potassium and sodium, and

studies have shown that SCG reduce the loss of potassium from 45 to 13% and sodium from 58 to 43% (Kasongo et al., 2011). These nutrients increase soil fertility and are equally important for healthy plant growth since it used as organic fertilizer on domestic agriculture (Cruz et al., 2012). While it is residual organic compounds can enhance the organic content, particularly N, and therefore fertility, indeed, and despite the absence of scientific evidence upon its effectiveness, or even its safety, the use of SCG in domestic agriculture is an increasing popular practice because it allow recovery of the soil structure and maintain soil fertility (Fan et al., 2006).

Chapter Three
Materials and Methods

3.1 Experimental site descriptions

Samples of LS were collected from four different local place of Marawa locality, Qarsa District, Jimma Zone, Oromia Regional National State and the samples of SCG were collected from eight different coffee houses at Jimma Town, Oromia Regional National State.

3.2 LS and SCG samples collection

Laterite soil (0-15 cm) using soil auger and spent coffee ground samples were collected and composite samples of the both LS and SCG were prepared by thoroughly mixing the collected samples 1:1 ratio independently. Before incubation study, collected LS and SCG samples were prepared for physicochemical analysis. The composite LS samples were air dried and ground in a wooden mortar to pass through a 2 mm sieve analysis and the composite SCG samples were dried in an oven at $60^{o}C$ until constant weight. For both LS and SCG samples, laboratory analysis was carried out at agriculture soil testing laboratory.

3.3 Characterization of LS and SCG

Particle size distribution was analyzed using hydrometer method (Bouyoucous, 1962) using sodium hexametaphosphate as dispersing agent. Soil textural class names were assigned based on the relative contents of the percent sand, silt, and clay separates using the soil textural triangle of the USDA. The chemical composition of LS was determined by using complete silicate analysis.

The pH of LS (LS:water ratio of 1:2.5) and SCG (SCG:water ratio of 1:5) was determined using pH meter as described by Thomas (1996). OC for both LS and SCG samples was determined by wet digestion method, following the assumptions that OM is composed of 58% carbon, and the conversion factor 1.724 was used to convert the OC to OM (Walkley and Black, 1934). EC of the LS and SCG were measured according to the method described by Peech (1965). CEC of the LS was determined by 1 M buffered ammonium acetate extraction method. Available P was

determined by (Murph and Riley, 1962) after extraction by Bray P II extractant and the available P in SCG was determined by a standard Ascrobic Acid blue color method.

3.4 Experimental Procedures

3.4.1 Effect of Incubation Time

Incubation study was conducted using LS and SCG. For this study, composite LS and SCG samples were putted in plastic cups separately. Four sorption treatment solutions containing 0, 20, 60 and 180 mg/L were prepared from KH_2PO_4. Two gram (2 g) of LS sample and 2 g of LS with varying of SCG (2:0.25, 2:0.5, 2:75 and 2:1) samples were weighed into labeled 50 ml plastic incubation cups and 25 ml portions of each of the four treatment prepared were added to each of the LS without SCG and the LS with SCG samples in the cups respectively. The whole experiment was duplicated and the mean data have been presented for duplicated data. The three drops of chloroform was added to each cup including LS and LS blended with SCG cups to prevent microbial growth. The cups were plugged and the samples were then incubated at room temperature for 1, 3, 7, 14 and 28 days making total of 80 samples (four concentrations x five incubation periods x two replicates).

Using a horizontal shaker, the samples were shaken at 120 oscillations per minute for one-hour. Two shakings were made at six hours interval per day. The samples were filtered using Whatman No 1 filter paper after 1, 3, 7, 14 and 28 days of incubation. The amount of P left in the clear solution was determined using the Ascorbic Acid blue color method. The P fixed (P_f) and percent P fixed were calculated using the following formula:

$$P_f = P_i - P_x \tag{3}$$

$$\%P_f = \frac{P_i - P_x}{P_i} \times 100 \tag{4}$$

Where P_f (mg/L) is the amount of P fixed; P_x (mg/L) is P in the fraction of treatment after incubation period (20, 60 and 180 mg/L); and P_i (mg/L) is initially added P concentration (20, 60 and 180 mg/L).

3.4.2 Effect of pH

To investigate pH effect 1 g composite of LS and LS blended with SCG (1:0.25, 1:0.5 and 1:0.75) were respectively weighed into a 50 ml separately. Then 20 ml of distilled water was added to samples and the pH of solution was adjusted at pH 4, 5,6,7,8,9,10 and 11 by dropping either HCL or NAOH. Twenty five ml (25 ml) of various concentrations of 20, 60 and 180 mg/L of P solution was added to mark up the mark of 50 ml. then tubes were placed in horizontal shaker to shake at a speed of 200 rpm for 1 h. The samples after shaking were filtered to obtained clear supernants and clear solution was determining using Ascorbic acid blue color method.

3.4.3 Effect of SCG Dose

To determine dose effect 2 g composite of LS and dose of SCG was added to the 50 ml of conical flask containing known concentration of phosphate solution (5 mg/L) and the dose of SCG varies from 0.5, 0.75, 1, 1. 5 and 2 g/L. Then solution in the conical flask was placed in horizontal shaker to shake at speed of 200 rpm for 1 h. after shaking the sample was filtered and determined by Ascorbic acid blue color method.

3.5 Data quality

The quality of the data was assured through reanalysis of samples or replicates the samples and calibrated by using standard operating procedures and duplicate data was averaged and mean ± SD was reported.

3.6 Data analysis and presentation

Origin Pro8 graphing software, Microsoft excel 2007 were used for data analysis. The analyzed data were presented in graph or table.

3.7 Plan for dissemination of findings

The findings of the study are presented to School of Civil and Environmental Engineering, Jimma Institute of Technology (Jimma University) and the complied report will be given to any responsible governmental institution or NOG for further investigation for practical application to alleviate the problem of P fixing. The results of this study will be published on a peer reviewed journal.

Chapter Four

Results

4.1 Characterization LS and SCG

The results of characterization analysis of for LS and SCG are given in Tables 1 and 2. According to the analysis result, LS is clayey in texture, moderately acidic in pH, medium in OC and OM contents, low in available P, not saline and has high CEC.

Table 4.1 Characterization of the experimental LS before incubation

Parameter	Unit		Value	Remarks
Texture	%	Sand	6	Clayey
		silt	24	
		clay	70	
pH (H$_2$O)			5.61	Slightly acidic
OC	%		2.106	Medium
OM	%		3.631	Medium
EC	ds/m		0.104	Non saline
CEC	cmol/kg		39.21	High
Available P	mg/kg		41.91	Low

The chemical compositions of SCG were: OC (47.57%), OM (82%) and available P (1745 mg/kg) (Table 4.2). The pH of SCG determined in water was 7.21and the EC was 0.54 ds/m (Table 4. 2).

Table 4.2 Characterization of the experimental SCG before incubation

Parameter	Unit	Values	Remarks
pH (H$_2$O)		7.21	Moderately basic
OC	%	47.59	Very high
OM	%	82	Very high
EC	ds/m	0.54	Non saline
Available P	mg/mg	1745	Very high

The results of laboratory analysis of chemical composition of LS are presented in Table 4.3. According to the analysis results show that about 64% of LS contain SiO_2 composition.

Table 4.3 Chemical compositions of LS

Parameter	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_3	TiO_2	H_2O	LoI
Percentage	63.52	13	9.78	0.78	< 0.01	0.82	< 0.01	0.38	0.18	1.79	1.25	8.25

The laboratory analysis of mineralogical composition of LS is presented in Table 4.4. According to laboratory results, the mineralogical compositions of LS were: kaolinite (20.94) and goethite (70.60).

Table 4.4 Mineralogical composition of LS

Parameter	Value
Kaolinite	20.94
Goethite	70.60

4.2 Phosphorus Fixation

The results of investigation of P fixing capacity LS are presented in Table 4.5. The results show that about 94% P was fixed in the first day of incubation from 20 mg/L P added into the solution.

Table 4.5 Amount of P fixed by LS from one to 28 day's incubation period.

Incubation (days)	20 mg P/L added P (mg/L) Recovered	Fixed	Fixed (%)	60 mg P/L added P (mg/L) Recovered	Fixed	Fixed (%)	180 mg P/L added P (mg/L) Recovered	Fixed	Fixed (%)
1	1.22	18.55	93.80	5.33	53.32	90.91	10.29	169.33	94.24
3	0.84	18.94	95.70	2.46	56.19	95.80	4.79	174.82	97.33
7	1.41	18.37	92.90	1.62	57.03	97.24	2.35	177.27	98.69
14	1.76	18.02	91.10	0.89	57.76	98.49	1.96	177.66	98.91
28	2.05	17.73	89.2	0.8	57.85	98.63	0.97	178.65	99.46

The results of laboratory analysis of P fixing of LS +SCG are presented in Table 4.6. The results show that about 53% P was fixed after twenty eight day of incubation from 20 mg/L P added into the solution.

Table 4.6 Amount of P fixed by LS blended with SCG from one to 28 days of incubation period.

Incubation (days)	20 mg P/L added P (mg/L) Recovered	Fixed	Fixed (%)	60 mg P/L added P (mg/L) Recovered	Fixed	Fixed (%)	180 mg P/L added P (mg/L) Recovered	Fixed	Fixed (%)
1	7.20	12.57	63.57	21.81	36.79	62.73	63.67	115.94	64.55
3	7.30	12.47	63.07	20.55	38.10	64.95	65.74	113.88	63.40
7	7.56	12.21	61.75	21.16	37.49	63.92	69.78	109.84	61.15
14	7.73	12.05	60.94	22.95	35.69	60.86	75.13	104.48	58.17
28	9.23	10.55	53.32	26.27	32.38	60.21	82.44	97.17	54.10

4.3 Effect of pH on P fixation

The results of investigation of LS pH effect are presented in Table 4.7. According to laboratory analysis the results show that about 76% P of fixed from 20 mg/L P added at pH6 into the solution.

Table 4.7 Amount of P fixed by LS

P in solution (mg/L)		pH solution							
		4	5	6	7	8	9	10	11
20	recovered	7.03	5.44	4.89	5.20	5.44	5.62	6.85	14.00
	fixed	12.97	14.56	15.11	14.80	14.56	14.37	13.15	6.00
	% fixed	64.83	72.82	75.57	74.00	72.79	71.86	65.77	30.00
60	recovered	7.48	5.46	4.73	5.75	6.28	7.17	8.02	40.56
	fixed	52.52	54.54	55.27	54.25	53.71	52.82	51.98	19.44
	% fixed	87.54	90.90	92.11	90.42	89.52	88.04	86.30	32.40
180	recovered	20.00	13.69	12.06	14.95	15.95	16.70	22.75	110.40
	fixed	160.00	166.31	167.94	165.34	164.05	163.29	157.25	54.72
	% fixed	88.89	92.39	93.30	91.86	91.14	90.72	87.36	38.68

The results of investigation of LS +SCG pH effect are presented in Table 4.8. The results show that about 43% P fixed was decreased at pH6 as compared with P fixed in LS from the same concentration (20 mg/L).

Table 4.8 Amount of P fixed by LS +SCG

P in solution (mg/L)		pH solution							
		4	5	6	7	8	9	10	11
20	Recovered	12.28	11.67	11.44	11.78	12.32	13.04	13.24	16.92
	Fixed	7.71	8.33	8.56	8.21	7.67	6.95	6.75	3.08
	% fixed	38.58	41.664	42.81	41.08	38.37	34.77	33.77	15.41
60	Recovered	29.49	25.93	24.61	26.39	27.41	27.82	29.17	48.66
	Fixed	30.51	34.07	35.39	33.61	32.59	32.18	30.82	11.34
	% fixed	50.85	56.78	58.98	56.01	54.31	53.64	51.38	18.90
180	Recovered	37.48	35.91	32.54	40.47	43.47	45.97	50.29	79.10
	Fixed	112.54	115.36	121.45	107.14	101.76	97.25	89.46	37.63
	% fixed	53.83	59.09	60.00	57.55	55.28	54.03	49.70	20.90

4.4 Effect of SCG dose

The results of laboratory analysis of effect of SCG dose are presented in Table 4.9. The results show that about 71% P fixed was decreased in 2 g of SCG dose.

Table 4.9 Effect of SCG dose

Dose (g/L)	20 mg P/L added			60 mg P/L added			180 mg P/L added		
	P (mg/L)		Fixed (%)	P (mg/L)		Fixed (%)	P (mg/L)		Fixed (%)
	Recovered	Fixed		Recovered	Fixed		Recovered	Fixed	
0.5	9.75	10.25	51.25	24.96	35.04	58.40	67.06	112.94	62.74
0.75	10.86	9.14	45.70	26.43	33.75	55.95	68.04	111.96	62.20
1	11.11	8.98	44.90	26.90	33.10	55.17	69.10	110.90	61.22
1.5	11.24	8.76	43.80	27.05	32.95	54.92	70.95	109.05	60.06
2	12.14	7.86	39.30	28.93	31.07	51.78	71.00	109.00	57.46

Chapter Five

Discussion

Characterization of LS and SCG: Laterite soils in the Karsa are clayey in texture, moderately acidic in pH, medium in OC and OM, low in available P, not saline in EC and high in CEC. In this study high clay content was observed in LS. The high clay content of the LS could increase P fixation due to its high surface area (Table 1.1). Havlin et al. (1999) report that the higher clay content of soil, the higher P fixation.

The collected SCG sample from different coffee houses has high OC, OM, and available P, moderately basic in pH and has no saline (Table 1. 2).

Based on the investigation, the high content of OM in SCG is observed that has the ability to moderate major changes in soil pH which available P was increased when SCG is applied as soil conditioner or amender. In this experiment available P was increase with increasing SCG dose. This increase might due to P solublizing effect of organic acids shielding of SCG on P adsorption sites, chelation of Al and Fe with complexing agents and its subsequent removal from a LS as well as a rise in LS pH. The study is in agreement with the study of Erich et al. (2002), Myungsu et al. (2004), found that application of compost can enhance the availability of soil P and even fixed P can be made available to plants after solubilization by soil microorganisms besides complexation of soluble Al and Fe by organic molecules.

Based on the result the Karsa LS is characeried by high chemical composition of SiO_2, Al_2O_3 and Fe_2O_3. in In this experiment high chemical composition of SiO_2 (63.52%), Al_2O_3 (13%) and Fe_2O_3 (978%) were observed respectively (Table 4.3). These chemical compositions show that high P fixation. Similar results were investigated by Ayodele and Agboola (1981). This shows that fixation increased with increase in amount of clay. This could also be an indication that the soils are made up of aluminosilicate clays of the layered structure (phyllosilicates), which have sites for adsorption of P. In addition, LS posses a great amount of Fe and Al oxides (Shaw, 2001; Ko et al., 2006).

Percent P fixed had also positive correlation with minralogical coomposition of LS which responsible for P fixation (Table 4.4). this might be due to the case of high clay minerals found in

LS which make a strong affinity for phosphate ions. This findig is in agreement with the study of (Tisdale et al.,1985).

Phosphorus fixation: P fixation generally increased with the amount of added P and time in LS (Table 4.5). When 20 mg/L of P was added in LS, fixation was very strong from the beginning and did not change much within 14 days. At 28 day's period, P fixed in LS was decreased and the amount of P available from LS + SCG remained significantly was increased this might be due to a satisfaction of some fixation sites by the ions produced after the decomposition of organic complex. The result is in agreement with the study of Fox and Comerford (1992) reported that OM decomposition produced lower molecular organic acids in soil.

P fixed was decreased from 20 mg/L P added with varying SCG addition (Table 4.6). This may due to high OM in SCG which competes with active sites of LS as a result P fixation could decrease. This finding is in agreement with the report of Erich et al. (2002) that deprotonation of carboxylate group (COOH), phenolic and alcoholic hydroxyls (OH) reduce soil acidity. The lowest fixation was obtained when 20 mg/L of P was added for LS and LS + SCG (Table 4.6). The low P-fixing capacity of the LS + SCG as compared to the LS may be due to the presence of more organic matter in the SCG. Organic molecules released on decomposition of organic matter form complexes with Fe and Al in the soil thereby blocking the sites which are mainly responsible for fixation of P in the soil (Juo and Fox, 1977; Ghosal et al., 2011; Brouwere, 2003). Banik et al. (2006) also report that addition of organic manure markedly increased the availability of P in the soil.

In addition, the decrease P fixation in LS +SCG could be associated to the fact that SCG has a large quantity of organic matter to the soil. This finding was similar with the study of (Kasongo et al., 2011) P fixation was reduced due to the increasing soil water holding capacity, alkalinity of soil humus with increasing SCG.

The percent P fixed in LS and LS +SCG we also correlated with LS properties at various incubation periods and concentrations of applied. Percent P fixed of LS had a negative correlation with organic carbon; this was similar with the studies on tropical savannah soils of Western Nigeria (Ayodele and Agboola, 1981) and the red and lateritic soils of West Bengal (Dolui et al., 1984). The negative correlation could be associated to the fact that the soil could be made up mainly of decomposing organic materials from citrates, tartrates, acetates, oxalates and malonates and they are the most anions effective to form complex ions with Ca^{2+}, Fe^{3+} and Al^{3+} and have greater

affinity for these cations than does the phosphate ion (Borie et al., 1983), however in LS +SCG this negative correlation was opposite as compared with LS in which the percent P fixed was decreased. This may be due to high contents of available P and OM in SCG. Again the organic matter could also be made up of fulvic acids which form loosely bound compounds hence P could be easily released with incubation period (Le Mare, 1991).

pH effect on P fixation: Based on pH effect P fixing capacity of LS show that 76% P of fixed from 20 mg/L P added at pH6 into the solution (Table 4.7). Lower pH values also elevate the concentration of Al in soil solution, taking up a greater proportion of the cation exchange sites and reducing base saturation. The amounts of P fixed increases at pH6 for LS in all phosphate concentration in solution was due to the presence of hydrogen (H^+) ions in a great extent and Al^{3+} ions in the soil solution which react with water and resulted the H^+ ions released and hydroxyl Al ions into the soil solution reduce the pH of the soil solution (Rowell, 1994). In addition, at lower pH values P fixed was increased due to high concentration of Al and Fe in soil solution which takes up a greater proportion of cation exchange sites and reduces base saturation (Ritchie, 1989).

Again based on pH effect of LS +SCG about 43% P fixed was decreased at pH6 as compared with P fixed in LS from the same concentration (20 mg/L). This might be due to more OM found in SCG when compared with the LS.

The lowest fixation values of P fixation in solution were obtained at pH11 for all concentration in LS +SCG as compared with LS. Similarly, precipitation of Al at high pH values could lock the exchange sites with positively charged Al hydrous oxides and fixation was not increasesd as compared with lower pH values. At high pH in the LS and LS +SCG after incubation period shows that P desorption. This result was similar with the study of (Gourango, 2007) P desorption increases due to the increasing negative charge on Al and Fe oxide surfaces because organic acids and soluble humic and fulvic acids released during the decomposition of OM which increases the desorption of added phosphate by competing for binding sites of the soil colloids. In addition to this, the amount of P fixed in LS and LS +SCG was found to be less at pH11 as compared to the other. This was due to repulsion between the more negatively charged PO_4^{3-} species and negatively surface sites at higher P values. This finding is in agreement with the report of (Sheng et al., 200).

As the study of this experiment indicates, the P fixation in LS and LS + SCG decreased from pH7 up to pH11. (Brandy andf Weil, 2002) found that adsorption of P by Fe and Al oxides declines with

increasing pH and decrease again in increasing pH due to interlayer hydroxyl aluminium polymers exist.

Another reason of P fixation decreases from pH7 to pH11 could be associated to the fact that, there was phosphate dissociation species which convert from $H_2PO_4^-$ to $H_2PO_4^{-2}$ (Hinsinger, 2001) found that adsorption at pH values above 6.8 sharp decreases in $H_2PO_4^{-2}$.

Effect of SCG dose: Effect of SCG dosage is studied and presented in Table 4.9. From the table it is observed that, as the dose of SCG increases, amount of P fixed decreases sharply and the attains the minimum. The point where maximum P fixed is attained is taken as optimum dosage at 2 g. In this experiment, available P was increased with increasing SCG dose .This increase might be due to high OM content of SCG. Hue (1992) and Abreha (2013) reported that adsorption of organic anions on hydrous Fe and Al surfaces, and release of hydroxyl ions from OM increase pH and reduce P fixation.

Chapter Six

Conclusions and Recommendations

6.1 Conclusions

Soil fertility is one of the main factors contributing to low productivity of crops and food insecurity in sub-Saharan Africa. Ethiopia is also one of the countries which located in this region and characterized by low available P sources. The Karsa soil indicates that low phosphorus availability. Hence, soil amendment is recommended.

With this work was possible to conclude that spent coffee ground can be used as fertilizer or soil conditioner agent in agriculture for LS amendment. The result indicated that high contents organic matter, available P and slightly basic conditions, the core factors suitable SCG as soil amendment. The study showed that the amount of P recovered at different incubations increase with increasing the dose SCG addition. Less than 63% of P fixation in the mixture of LS and SCG was decreased after one day of incubation.

Application of SCG is recommended for LS to increase soil fertility. P could therefore be responsible in decrease of P fixation of LS.

6.2 Recommendations

The following recommendations are made, based on the results from the study:

1. As blending of SCG with LS decreases P fixing, the SCG can be applied to soil to increase the availability of P for plants.
2. Soil pH has no significant effect on the P fixing of the soil amended with SCG. Thus, application of SCG onto soil may avoid the need for pH adjustment to increase P availability.
3. The investigation is carried out at laboratory conditions and set up. Thus, further field investigation of SCG for practical application is required.

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Appendix

Appendix Figure4. 1Amount of P fixed in both LS and LS +SCG after incubation
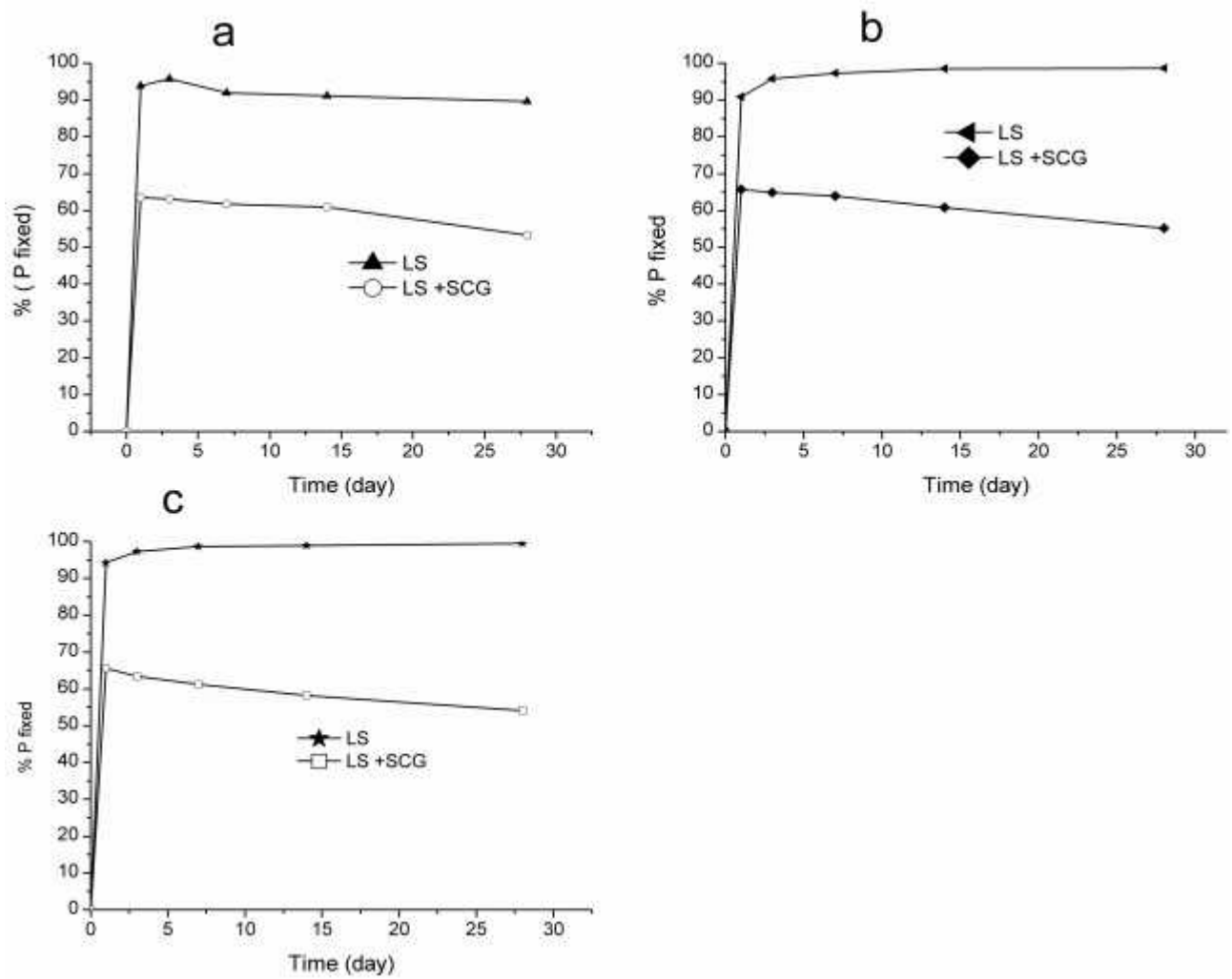
Appendix Figure 4.2Amount of P fixed in LS and LS +SCG at different pH
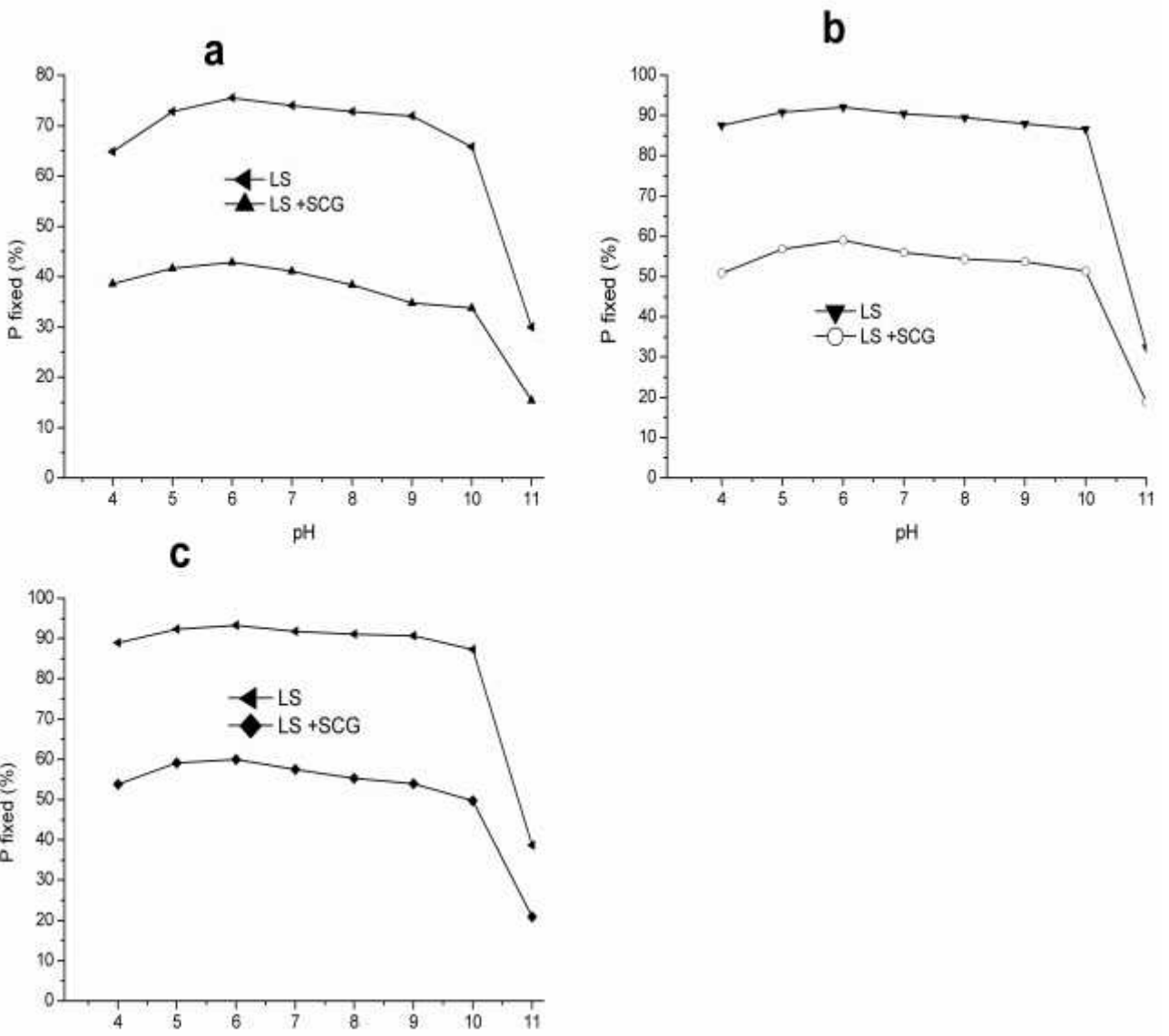
Appendix Figure 4.3 Effect of SCG dose