

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI,
GHANA

COLLEGE OF SCIENCE

DEPARTMENT OF CHEMISTRY

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PHOSPHORUS ADSORPTION ISOTHERMS OF SOME SELECTED SOILS FROM THE
EASTERN REGION OF GHANA

A thesis submitted to the Department of Chemistry, Kwame Nkrumah University of Science
and Technology in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

Analytical Chemistry

By

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(BSc. Chemistry)

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DECLARATION

I hereby declare that this submission is my own work towards the MSc. and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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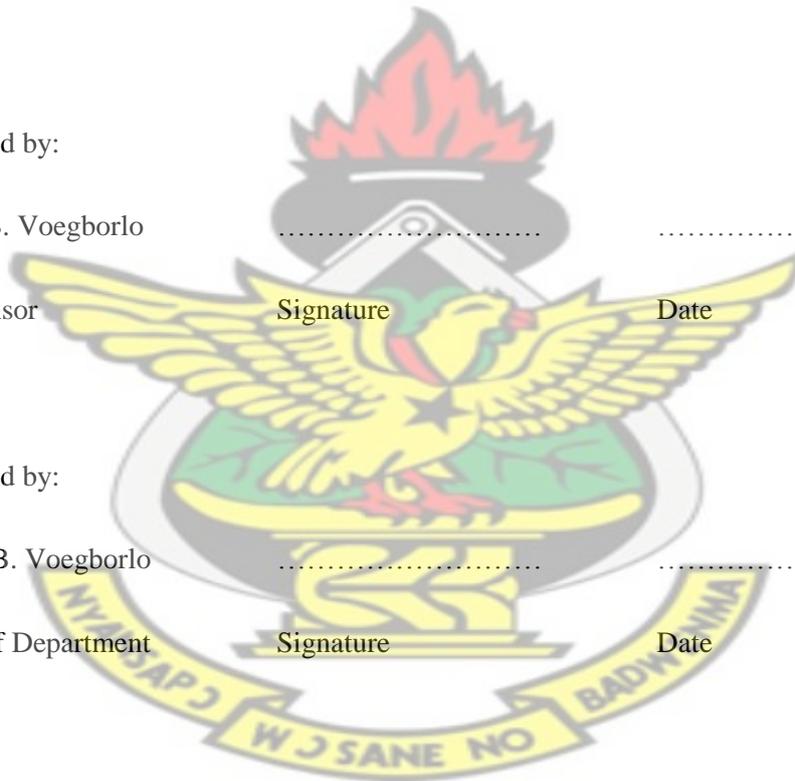
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DEDICATION

This work is dedicated to the Almighty God for His manifold mercies and love.

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ACKNOWLEDGEMENT

First to the Almighty God for His unmerited favour on my life, secondly to my supervisor, Dr. R. B.Voegborlo for his profound words of encouragement. Mr. Selorm Agorku, Mr. William Appau, Mr. George Atongo, Nana Baah and other members of staff of the Chemistry and Biochemistry Departments, I say a big thank you. To my dad I say a special AYEKOO.

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ABSTRACT

Phosphorus (P) sorption in soils is a key process governing its availability to crops and environmental consequences. As a result of the high P fixation (low soil solution P concentration) in soils worldwide, crop yields are often low. In view of this fact, this study was initiated to determine the P sorption characteristics of some soils and derive parameter estimates relevant in the prediction and management of P as well as their relationship to the properties of the soils. Twelve soil samples were obtained from the Eastern Region of Ghana for this study. Measurement of P sorption was conducted by equilibrating air dried soil (<2 mm) in 0.2 M CaCl₂ solution containing various concentrations of P. Phosphorus concentrations in the equilibrium solution were determined by the molybdenum blue method. The amount of P sorbed by the soils differed among the various soils. Differences in P- adsorption were greatly influenced by soil properties like soil organic carbon (SOC), soil pH, amounts of calcium and aluminium and the clay content. Soil from Huhunya which was virgin, adsorbed the greatest P, and the least P was also adsorbed by soil from a plantain farm in Huhunya. Phosphorus sorption data for soils was fitted to the Langmuir, Freundlich and Temkin isotherm equations. Phosphate adsorption was well described by the three isotherm equations but the Langmuir adsorption isotherm provided the best fit to the experimental data. The three parameters derived from the Langmuir isotherm are the adsorption maximum (K_{max}), bonding capacity (b) and the maximum buffering capacity. Adsorption maximum and bonding capacities estimated ranged from 109.89 $\mu\text{g/g}$ to 625.00 $\mu\text{g/g}$ with an average value of 211.61 $\mu\text{g/g}$ and from 0.124 mL/ μg to 0.692 mL/ μg with an average value of 0.285 mL/ μg respectively. Maximum buffering capacity also ranged from 19.235 to 294.125 with an average value of 72.55. The sorption capacity (a) and sorption energy (n) were

estimated from the Freundlich equation and they ranged from 37.601 to 224.388 $\mu\text{g/g}$ and 2.721 to 5.988 with average values of 82.965 $\mu\text{g/g}$ and 3.930 respectively. Buffering capacity (B) which was estimated from the Temkin equation ranged from 16.915 to 103.350, with an average value of 37.991. It was realized that virgin soil from Huhunya would require the most P fertilizer. The least P fertilizer would be required by soil from the plantain farm (HP). Correlation analysis showed significant relationship between some soil characteristics and the sorption parameters derived from the three equations. There is however the need for inclusion of more soil chemical, physical and mineralogical properties in predicting soil P-adsorption to enhance reliability of information.



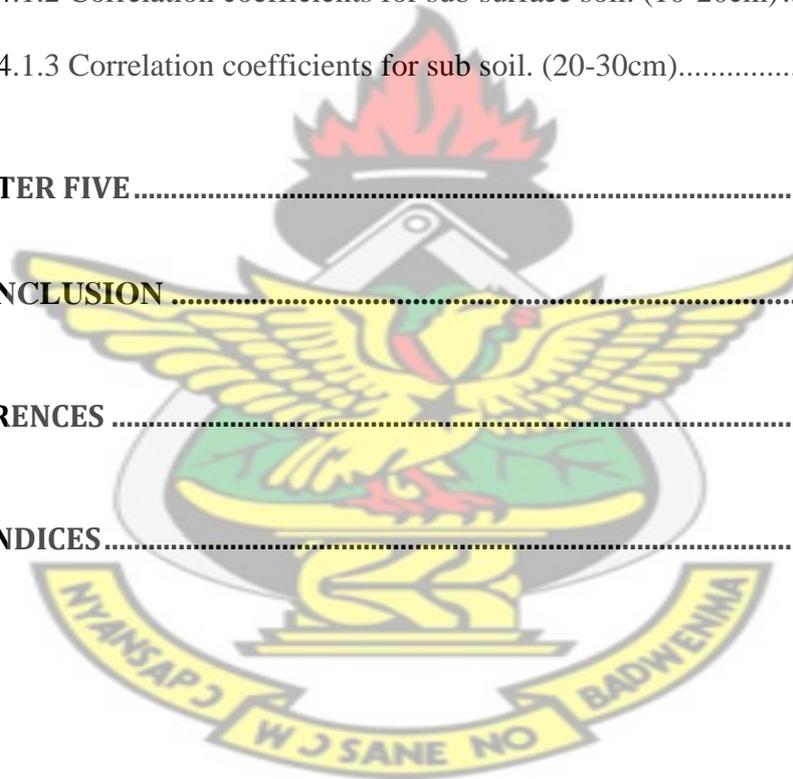
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CHAPTER ONE

1. INTRODUCTION

Phosphorus (P) is an important naturally occurring element in the environment that can be found in all living organisms as well as in water and soils. It is an essential component for many physiological processes related to proper energy utilization in both plants and animals. It is a component of key molecules such as nucleic acids, phospholipids, and adenosine triphosphate (ATP). Phosphorus is also a critical element in natural and agricultural ecosystems throughout the world (Onweremdu, 2007), as its limited availability is often the main constraint for plant growth in highly weathered soils of the tropics (Bunemann *et al.*, 2004). Consequently, plants and animals cannot grow without a steady supply of this nutrient (Theodorou and Plaxton, 1993). In plants it is a macronutrient, making up about 0.2% of a plant's dry weight. It is required for root development and strength of straw in cereals (Tisdale *et al.*, 1990)

Even though soils may contain several hundred to thousand kilogrammes of phosphate per hectare, much of the phosphate in soils may not be available to growing plants. Its availability is controlled by sorption, desorption and precipitation processes in the soil (Eghball *et al.*, 1990; Sims *et al.*, 1998). Phosphorus usually has a high affinity for soil, resulting in slow downward movement through the soil matrix (Eghball *et al.*, 1990; Sims *et al.*, 1998) or laterally through interflow. Significant amounts of P may move by preferential flow paths (Jensen *et al.*, 1998; Simard *et al.*, 2000) with little adsorption to the soil matrix (Jensen *et al.*, 1998).

Sorption or fixation is the process by which phosphorus binds to the soil, thereby becoming unavailable for leaching or run off. The adsorption of phosphate is the process in which phosphate ions in solution react with atoms on the surface of soil

particles (Abedin and Salaque, 1998). This is an important property affecting both the fate of phosphate fertilizer and the availability of phosphate to plants.

Investigations on phosphate adsorption have mainly been centered on two major areas, namely the mechanism of phosphate adsorption and the identification of phosphate reactive sites. Understanding of the P adsorption mechanism is vital for improving efficiency of phosphate fertilizer while the latter is essential to evaluate intensity of adsorption and understanding the various processes associated with the phenomenon.

Compounds of iron and aluminum particularly the oxide and hydroxide forms and those of calcium have been identified as the principal soil constituents active in phosphate adsorption (Holford and Mattingly 1975; Parfitt, 1978; White, 1980). This is particularly true for tropical upland soils where deficiency of P is the most prevalent initial constraint to plant growth (von Uexkull, 1989).

Soil P is found in different pools, such as organic and mineral (inorganic P). It is important to emphasize that 20 to 80% of P in soils is found in the organic form; of which phytic acid (inositolhexaphosphate) is usually a major component (Richardson, 1994). The remainder is found in the inorganic fraction containing several mineral forms of P (Holford, 1997).

Because soil solution contains very low concentration of P as compared to plant requirements, continuous replenishment of this pool to avoid P deficiency is necessary. The labile P fraction serves this purpose. The labile soil P consists of P weakly adsorbed onto soil surfaces. This fraction is in equilibrium with solution P and is considered to be potentially available for plants use (Larsen *et al.*, 1965). The concentration of P in this fraction could be 10 to 100 times greater than that in

solution (Mengel and Kirkby, 1982). Depending on time and soil P characteristics, the labile pool can become more stable and move into a non-labile pool (Barrow and Shaw, 1975). The non-labile P is strongly held on and within the clay lattices or is occluded by some other precipitation re-crystallization reaction. This fraction reverts slowly into labile P, and is considered to be not available to plants.

When the soil P equilibrium is disturbed by adding fertilizer, reaction between fertilizer and soil takes place in two steps: a rapid step leads to adsorption of P and a slow reaction converts P to a more firmly held form (Barrow, 1974; 1978; Barrow *et al.*, 1981).

The uncertainties about P-chemistry in soils are due to its strong interaction with many organic and inorganic solid phases, continual uptake by plants and micro-organisms, continual return from organic decay and slow reaction rates (Isirimah *et al.*, 2003). P-adsorption capacities of soil are influenced by Fe and Al oxides (Hakim, 2002), exchangeable calcium and magnesium, soil texture, moisture content, temperature, porosity, pH, ionic strength and hydraulic conductivity (Bubha *et al.*, 2003). It has also been reported that the land utilization type influences P-adsorption capacity (Amapu *et al.*, 2000).

Phosphorus deficiency problems are common in well-weathered oxisols and ultisols because of strong acidic reactions and abundance of Al and Fe ions (Saleque *et al.*, 2004), and the situation can be worsened with inappropriate P management (Saleque *et al.*, 1998). Owusu Bennoah and Acquaye (1989) studied the phosphate sorption characteristics of some Ghanaian soils and found that phosphate sorption was highly correlated with the soil properties in the reducing order: Al_2O_3 , clay content, free Fe_2O_3 and organic carbon.

As a particle of fertilizer comes in contact with the soil, moisture from the soil will begin dissolving the particle. Dissolution of the fertilizer increases the soluble phosphate in the soil solution around the particle and allows the dissolved phosphate to move a short distance away from the fertilizer particle usually by diffusion (Grant and Heaney, 1997).

Movement is slow but may be increased by rainfall or irrigation water flowing through the soil. As phosphate ions in solution slowly migrate away from the fertilizer particle, most of the phosphate will react with the minerals within the soil. Phosphate ions generally react by adsorbing to soil particles or by combining with elements in the soil such as calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe), and forming compounds that are solids. The adsorbed phosphate and the newly formed solids are relatively available to meet crop needs.

Gradually reactions occur in which the adsorbed phosphate and the easily dissolved compounds of phosphate form more insoluble compounds that cause the phosphate to become fixed and unavailable. The mechanisms for the changes in phosphate are complex and involve a variety of compounds. In alkaline soils (soil pH greater than 7) Ca is the dominant cation (positive ion) that will react with phosphate. A general sequence of reactions in alkaline soils is the formation of dibasic calcium phosphate dihydrate, octocalcium phosphate, and hydroxyapatite (Donald *et al.*, 1999). The formation of each product results in a decrease in solubility and availability of phosphate.

In acidic soils (especially with soil pH less than 5.5), Al is the dominant ion that will react with phosphate. In these soils the first products formed would be amorphous Al and Fe phosphates, as well as some Ca phosphates. The amorphous

Al and Fe phosphates gradually change into compounds that resemble crystalline variscite (an Al phosphate) and strengite (an Fe phosphate).

The various forms and phase transformation reactions of P complicate the prediction of transport (Grant and Heaney, 1997). Evidence of dissolved organic P loss in leachate is mixed. Bowman *et al* (1967) concluded that organic P tended to accumulate on the surface with little downward movement through the root zone. However long-term field trials using manure application concluded that organic P actually travelled deeper in the soil profile than the inorganic forms (Sims *et al.*, 1998). Movement and loss of P have been correlated with redistribution of dissolved organic matter in soils (Donald *et al.*, 1999), streams wetlands and cropped and grassed lands (Ekholm *et al.*, 1999)

Due to all these complications, many studies on the P dynamics in various soils have been carried out but the most pertinent issue is to know how much of phosphorus in soil can be made available to growing plants and how much is lost to water bodies through leaching and runoff with environmental consequences.

Phosphorus fertilizer is an expensive input and its use efficiency by crops may range from 10-25% (Bahl and Singh, 1986). The high P content of soil and consequential loss of excess or un-adsorbed P from soil to water causes eutrophication. To determine eutrophication risk, there is a need to assess the environmental utility of conventional tests for P in soil. Sims *et al* (2000) reported that conventional soil tests clearly do not characterize site hydrology or nutrient management practices and cannot identify the risk of direct loss of P in runoff from fertilizers and organic wastes applied to the soil surface, thus making risk-management decisions based solely on agronomic soil test P a flawed approach.

An effective soil test can help to predict the fertilizer requirement of crops. However, conventional soil tests provide information only about plant available P (Fixen and Grove, 1990) and do not estimate the amount of P fertilizers needed unless calibrated for the particular soil under test (Fox and Kamprath, 1970). Furthermore these tests do not correctly predict the fertilizer-P requirement for a particular soil – crop system (Rashid and Hussain, 1988). To estimate eutrophication risk, it may be necessary to substitute current soil test methods with a new approach for assessing the capacity of a soil to retain P against leaching (Edwards and Withers 1998; Sims *et al.*, 2000).

Consequently, P sorption isotherms, which relate concentration of P in soil solution with P sorbed by the soil, have been used to correctly predict the P fertilizer requirement of crops (Beckwith, 1965; Fox and Kamprath, 1970; Shah *et al.*, 2003; Okunola *et al.*, 2010).

The soil parameters which play a major role in P flux to plant roots include: (i) the measured phosphate concentration in solution known as intensity (I), (ii) quantity (Q), which is the phosphate adsorbed, (iii) buffering capacity ($\Delta Q / \Delta I$) and (iv) mobility factors (Dalal and Hallsworth, 1976). The quantitative description of the Q / I relationship (at an equilibrium concentration) is known as the buffering capacity of the soil and is important for predicting the fertilizer-P requirements of the soil (Fox and Kamprath, 1970). It is the indication of the ability of the soil to replace a unit change in soil solution P and maintain a productive solution concentration. The soil P buffering capacity may be the limiting factor in P uptake (Holford, 1976; Nair and Mengel, 1984). Phosphorus buffering capacities are derived from adsorption isotherm plots (Holford- 1976, Parfitt, 1978; Olsen and Khasawneh, 1980).

Such relationships for P in the soil system can be obtained by fitting data to suitable isotherm equations, such as the Langmuir (Bolster and Hornberger, 2007; Jiao *et al.*, 2007; Jiao *et al.*, 2008), Freundlich equation (Zhang and Selim, 2007; Bolster and Hornberger, 2007; Jiao *et al.*, 2008) and the Temkin equation (Anghinoni *et al.*, 1996; Ioannou *et al.*, 1998),

The adsorption isotherm is the most useful experimental procedure in the study of interaction of anions with oxides or soils and has been used by many scientists to measure the adsorption capacity of soils (Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Barrow, 1970, 1978). The adsorption capacities of soils have been important criteria in soil classification (Rajan, 1973; Breeuwsma *et al.*, 1986).

The adsorption curves provide an adequate basis for estimation of P requirements across a diversity of soils and environment (Van Der Zee *et al.*; 1979). Adsorption isotherms have an advantage over conventional methods of soil testing, because the isotherms consider both intensity and capacity factors (Rajan, 1973; Tiarks, 1982).

Adsorption isotherms are lines or curves relating the amount of substance at an interface to its concentration at equilibrium in the medium in contact with the interface at a constant temperature. They are used to determine and predict the P sorption maxima and bonding energies for soils with different properties and utilization types.

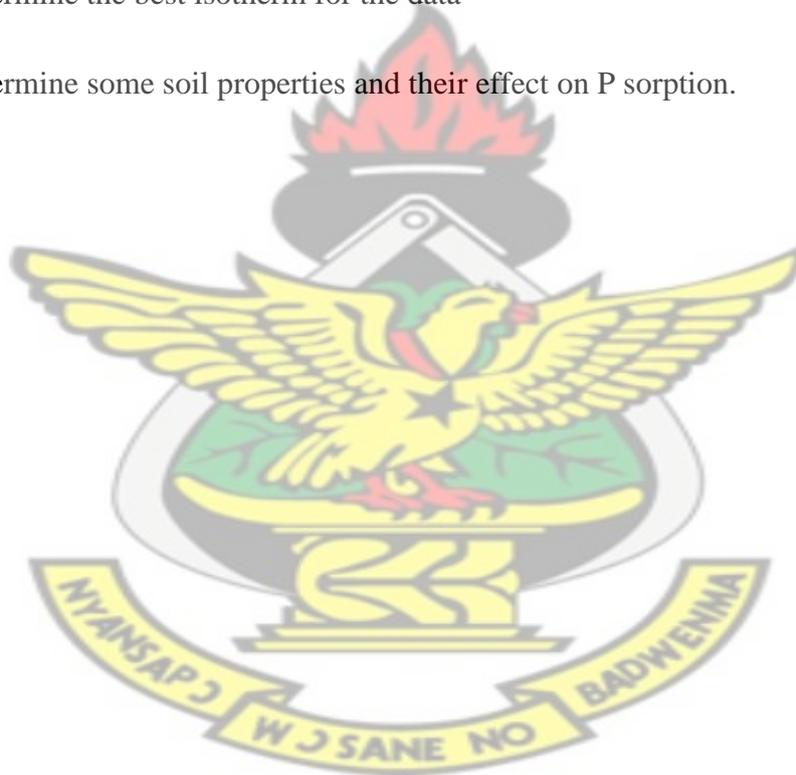
Whereas studies have been carried out worldwide on P sorption, (Woodruff and Kamprath, 1967; Olsen and Watanabe, 1957; Fox and Kamprath, 1970; Singh and Tabatabai, 1977; Zhang and Selim, 2007; Bolster and Hornberger, 2007; Jiao *et al.*, 2008, Ahmed *et al.*, 2008; Okunola *et al.*, 2010), little attention has been paid to it in Ghana.

This study seeks to determine the phosphate sorption characteristics of some soils from the Eastern region of Ghana

OBJECTIVES OF RESEARCH

The objectives of this study are to:

1. Study P sorption of some selected soils.
2. Obtain sorption isotherms so as to evaluate the phosphate requirement of the selected soils
3. Determine the best isotherm for the data
4. Determine some soil properties and their effect on P sorption.



CHAPTER TWO

2. LITERATURE REVIEW

2.1 History of Phosphorus

The element Phosphorus (P) was first discovered by the German alchemist Hennig Brand in 1669 when he attempted to create the philosopher's stone from his own urine. Because Phosphorus emitted a faint glow when exposed to oxygen, it was named after the planet Venus (the morning star) which was also commonly called the light bearer.

2.2 Properties

Phosphorus (P) is found in group 15 of the periodic table. It has an atomic weight of 30.973761 and is solid at 298 K and 1000 kPa. It has a density of 1.82 g/mL at 293.2 K, a melting point of 317.4 K and a boiling point of 553.2 K.

Phosphorus has several forms (allotropes) that have strikingly different properties. The two most common allotropes are white phosphorus and red phosphorus. Red phosphorus is an intermediate phase between white and violet phosphorus. Another form, scarlet phosphorus, is obtained by allowing a solution of white phosphorus in carbon disulfide to evaporate in sunlight. Black phosphorus is obtained by heating white phosphorus under high pressures (about 12,000 atmospheres). In appearance, properties, and structure, it resembles graphite: being black and flaky, a conductor of electricity, and a puckered sheet of linked atoms. Another allotrope is diphosphorus, which contains a phosphorus dimer as a structural unit and is highly reactive.

White phosphorus has two forms, low-temperature β form and high-temperature α form. White phosphorus is the least stable, the most reactive, most volatile, least

dense, and most toxic of the other allotropes. Contact with skin causes severe burns. The toxicity of white phosphorus led to its discontinued use in matches. White phosphorus is thermodynamically unstable at normal condition and will gradually change to red phosphorus.

Red phosphorus may be formed by heating white phosphorus to 523.2 K or by exposing white phosphorus to sunlight. Phosphorus after this treatment exists as an amorphous network of atoms that reduces strain and gives greater stability; further heating results in the red phosphorus becoming crystalline. Therefore red phosphorus is not a certain allotrope, but rather an intermediate phase between the white and violet phosphorus, and most of its properties have a range of values. Red phosphorus does not catch fire in air at temperatures below 533.2 K, whereas white phosphorus ignites at about 300.2 K.

Violet phosphorus is a thermodynamic stable form of phosphorus that can be produced by day-long temper of red phosphorus above 773 K. Black phosphorus is the least reactive allotrope and the thermodynamic stable form below 823.1 K. It is also known as β -metallic phosphorus and has a structure somewhat resembling that of graphite.

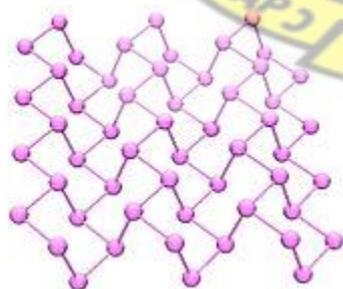


Fig 1.1 Black phosphorus

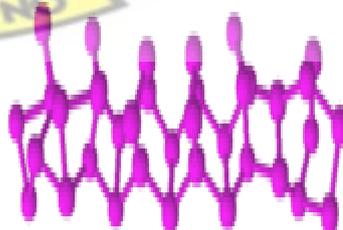


fig 1.2 Red phosphorus

2.3 OCCURENCE

Due to its reactivity with air and many other oxygen-containing substances, phosphorus is not found free in nature but it is widely distributed in many different minerals. Phosphate rock, which is partially made of apatite (an impure tri-calcium phosphate mineral), is an important commercial source of this element. Large deposits of apatite are located in the Arab states, China, Russia, Morocco, Florida, Idaho, Tennessee, and Utah.

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2.4 BIOLOGICAL ROLE

Phosphorus is a key element in all known forms of life. Inorganic phosphorus in the form of the phosphate PO_4^{3-} plays a major role in biological molecules such as DNA and RNA where it forms part of the structural framework of these molecules. Calcium phosphate salts assist in stiffening of bones. Living cells also use phosphate to transport cellular energy in the form of adenosine triphosphate (ATP). Nearly every cellular process that uses energy obtains it in the form of ATP. ATP is also important for phosphorylation, a key regulatory event in cells.

Low-phosphate syndromes are caused by malnutrition, failure to absorb phosphate, and metabolic syndromes that draw phosphate from the blood (such as re-feeding after malnutrition) or pass too much of it into urine. All are characterized by hypophosphatemia, which is a condition of low levels of soluble phosphate levels in the blood serum, and therefore inside cells. Symptoms of hypophosphatemia include muscle and neurological dysfunction, and disruption of muscle and blood cells due to lack of ATP. Too much phosphate can lead to diarrhoea and calcification

(hardening) of organs and soft tissue, and can interfere with the body's ability to use iron, calcium, magnesium, and zinc.

Phosphorus is an essential macromineral for plants, which is studied extensively in order to understand plant uptake from soil systems. Phosphorus deficiency symptoms most often occur in seedlings and young plants. Phosphorus is mobile within the plants; it is translocated from the older, first formed tissue to the growing points. This causes the deficiency symptoms on the lower leaves. Deficiency of phosphorus generally causes stunted growth, dark green colour associated with a purplish colour in the seedling stage. Inadequate supply of phosphorus generally causes delay in crop maturity and seed formation.

In ecological terms, phosphorus is often a limiting factor in many environments; i.e. the availability of phosphorus governs the rate of growth of many organisms. In ecosystems an excess of phosphorus can be problematic, especially in aquatic systems, causing problems like eutrophication and algal bloom.

2.5 PHOSPHORUS IN THE ENVIRONMENT

2.5.1 White phosphorus

White phosphorus enters the environment when industries use it to make other chemicals and armies use it for ammunition. Through discharge of waste water, white phosphorus ends up in surface waters.

White phosphorus is not likely to spread because it reacts with oxygen fairly quickly. When phosphorus ends up in air, it will react with oxygen right away to be converted into less harmful particles.

2.5.2 Phosphates

Phosphorus can be found in the environment most commonly as phosphates. Phosphates have many direct effects on organisms. The effects are mainly consequences of emissions of large quantities of phosphate into the environment due to mining and crop cultivation. During water purification phosphates are not normally removed properly, so they can spread over large distances when found in surface waters.

Due to the constant large amount of phosphates released into the environment, the phosphorus cycle is perturbed.

2.6 FORMS OF SOIL PHOSPHORUS

The various forms of phosphorus in soils can be classed generally as inorganic and organic, depending upon the nature of compounds in which it occurs. The inorganic forms of phosphorus in soil are frequently greater than organic forms. It is important to emphasize that 20 to 80% of P in soils is found in the organic form, of which phytic acid (inositol hexaphosphate) is usually a major component (Richardson, 1994). An exception to this would be the phosphorus contained in predominantly organic soils. In addition, the organic phosphorus content of mineral soils is usually higher in the surface horizon than it is in the subsoil because of the accumulation of organic matter in the upper part of the soil profile.

2.6.1 Inorganic soil phosphorus

The primary and secondary minerals, which are crystalline and have been identified by optical and X-ray methods, account for only a small portion of the inorganic

phosphate in soil. Voluminous literature is available on the distribution of various forms of inorganic phosphorus. There are certain soil properties which regulate the distribution of inorganic forms of phosphorus. These are pH, soluble and exchangeable P-reactive cations (iron, aluminium, calcium and magnesium), and the nature and surface area of soil particles.

In all soils, P will occur in the adsorbed phase on the surfaces of iron and aluminium hydroxides and other clay minerals. However, in soils most of the inorganic phosphorus occurs in the clay fraction as salts of orthophosphoric acid.

Attempts have been made to classify inorganic soil phosphorus into different compounds according to their extractability in various reagents (Chang and Jackson, 1957). However, such a classification appears to be arbitrary and does not reveal their true nature.

A great deal of knowledge concerning the nature of soil phosphorus is based on solubility product principles. Phosphorus forms insoluble compounds with iron and aluminium at low pH, more soluble compounds with calcium and magnesium at pH values near neutrality and insoluble compounds with calcium at higher pH values (Tisdale. *et al.*, 1985). There is a wide range of solubility of these various phosphate compounds and their availability to crops is usually the greatest within the pH range of about 6 to 7 for most agricultural soils.

The inorganic phosphorus compounds are mainly divided into two groups: Phosphorus compounds of calcium and magnesium and phosphorus compounds of iron and aluminium.

2.6.1.1 Calcium and Magnesium Phosphates

They occur in soils in several forms and the most important compounds are given as follows:

- a. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, monocalcium phosphate, which is the water-soluble component of superphosphate and reacts in soil to form less soluble products.
- b. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 , dicalcium phosphate, both hydrated and the unhydrated forms are slightly soluble in water.
- c. $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, Octacalcium phosphate.
- d. $\text{Ca}_3(\text{PO}_4)_2$, tricalcium phosphate.
- e. $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, hydroxyapatite and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}$, fluorapatite and
- d. $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, struvite which is alkaline and water-soluble.

Dicalcium phosphate, octacalcium phosphate and hydroxyapatite are the principal crystalline phosphates that have been identified in soil (Tisdale *et al.*, 1985). The native phosphorus in soils originated largely from disintegration of rocks containing the mineral apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl,OH})_2$. Apatite has also been reported as a common soil mineral by Shipp and Matelski (1960). Hydroxyapatite has been reported to be a stable form over a wide range of pH (Larsen, 1967). The apatite in its primary form has little or no significance in supplying phosphate to plants, because of very low solubility and rate of solubilization (Wild, 1988).

The phosphorus concentration in calcareous soils does not correspond to any one mineral species. It may be controlled by octacalcium phosphate in some soils or by hydroxyapatite in other soils. The hydroxyapatite in soil invariably contains some carbonate ions, which makes it chemically more reactive. The presence of

octacalcium phosphate has been reported in soils which have been limed and fertilized with phosphates (Webber and Mattingly, 1970).

Baifan and Yichu (1989) suggested a systematic fractionation scheme for inorganic phosphates in calcareous soils, in which they classified calcium phosphate into dicalcium phosphate, octacalcium phosphate and apatite types. They also suggested that these forms are interchangeable. Some other workers reported the fractionation of inorganic phosphorus in the calcareous soils as a series of calcium phosphates with complex physico-chemical reactions and different availability to plant growth (Williams *et al.*, 1967 and 1971, Syers *et al.*, 1972 and Hooker *et al.*, 1980).

The availability of P from various inorganic compounds was compared by Tisdale *et al.* (1985). It was revealed that there was the highest P availability from struvite $MgNH_4PO_4 \cdot 6H_2O$ as compared to mono or dicalcium phosphate. In soils containing large quantities of magnesium, a number of insoluble magnesium phosphate compounds such as dimagnesium phosphate trihydrate, trimagnesium phosphate and struvite may form. However, these magnesium phosphates are more soluble than dicalcium phosphate and octacalcium phosphate.

2.6.1.2 Iron and Aluminium Phosphates

A number of aluminum and iron phosphate minerals have been reported to occur in soils. The most common aluminum phosphates are wavellite ($Al_3(PO_4)(OH)_3 \cdot 5H_2O$) and variscite ($AlPO_4 \cdot 2H_2O$). The occurrence of variscite has been postulated in soil of slight acidity (Lindsay and Moreno, 1960). At higher pH values, variscite dissolves incongruently, whereby a more basic solid phase of aluminum hydroxy phosphate is formed (Taylor and Gurley, 1964). This material probably controls

phosphorus concentration in solution in acid soil by forming a surface complex on variscite. However, in pure systems, where the pH of the equilibrium solution is less than 3.1, the solubility product of variscite controls the phosphorus concentration in solution (Chakravarti and Talibudeen, 1962).

The most common iron phosphate is strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). Chakravarti and Talibudeen (1962) concluded that a compound approximating to the composition of strengite may occur in temperate soils in the pH range of 3.8 to 4.2, whereas in tropical soils strengite coexists with hydrated iron oxide from pH 3.8 to 6.7

The least soluble compounds at acidic pH are variscite and strengite (Tisdale *et al.*, 1985). Strengite is known to crystallize more rapidly when the iron phosphate is formed. The less crystalline aluminium phosphate has greater surface area which is more favorable for release of phosphorus into the soil solution. Under very acid conditions minerals of the variscite and strengite groups are precipitated (Wild, 1988).

2.6.2 Organic Soil Phosphorus

The amounts of organically held phosphorus vary greatly among soils. Organic phosphorus content of soil occurs from traces in arid soils to several hundred mg/kg in thick forest soils. It is roughly related to organic matter contents both among soils and within the soil profile. Hence the circumstances that lead to increased soil organic matter also generally lead to increased organic phosphorus contents. The organic phosphorus contents of the soils throughout the world range between 7 to 1056 mg/kg of soil (Campbell and Racz, 1975).

Most naturally occurring organic forms of phosphorus are esters of orthophosphoric acid and numerous mono and di-esters have been characterized. According to Tisdale *et al.*, (1985) these organic phosphorus esters have been divided into five classes of compounds: inositol phosphates, phospholipids, nucleic acids, nucleotides and sugar phosphates. The first three are the dominant groups in soils.

It is generally assumed that soil organic phosphorus is derived directly or after biochemical transformations from crop and animal residues, in which part of the phosphorus is present in organic compounds. The phosphate added as fertilizer is converted to organic forms in soil under young grassland due to increased root production and leaf decay added to the soils (Wild, 1988). The importance of the mineralization of organic phosphorus compounds for crop nutrition is probably universal. But it is greatest at high soil temperatures because of high mineralization rates. Mineralization of organic P may release considerable amounts of inorganic P in favourable conditions of moisture, pH and root activity.

2.7 SOIL FACTORS AFFECTING P UPTAKE

According to Kamprath and Watson (1980) the factors affecting the supply of P to plants are the amount of soil P (quantity), the concentration of soil solution P (intensity), and movement of P to roots (diffusion). In any assessment of the available P in soil by chemical tests, one needs to consider the relationship between quantity, intensity and diffusion and factors influencing availability of these components of P to plants.

2.7.1 Phosphate Buffering Capacity

The P equilibrium between solid phase and solution phase is characterized by phosphate buffering capacity of a soil. This is the ability of a soil to maintain its P concentration in solution as P immobilized by soil through various processes or as P is added by fertilization. Thus the availability of soil phosphate is described by both intensive and extensive parameters which are determined by the concentration of phosphorus in soil solution (I) and quantity of phosphate adsorbed on the soil solids (Q) respectively. These two parameters determine the buffering capacity of soil (Barrow, 1967; Holford, 1976), which regulates the resistance of I and Q to change when phosphate is added or disturbed by the system (Holford and Mattingly, 1976a).

The buffering capacity of a soil is the slope of the adsorption isotherm at some arbitrary concentration, which may reflect the actual P concentration found in the solution (Beckett and White, 1964), or theoretical P concentration sufficient for plant growth (Ozanne and Shaw, 1967), or the calculated maximum slope at zero concentration (Holford and Mattingly, 1976a). It is an indication of the ability of the soil to replace a unit change in soil solution P and maintain a productive solution concentration. The soil P buffering capacity may be the limiting factor in P uptake (Holford, 1976; Nair and Mengel, 1984).

Soils with high phosphate adsorption maxima have higher phosphate buffering capacity than those with low phosphate adsorption maxima (Rajan, 1973). The higher or stronger the buffering capacity, the larger the proportion of P in solid phase relative to solution phase; increasing buffering capacity also lowers the rate of dissolution or desorption of P from the solid phase and vice versa (Holford, 1989).

According to Kamprath and Watson (1980) the buffering capacity of acid and neutral soils is a function of the amounts and crystallinity of hydrated oxides of Fe

and Al, whereas in calcareous soils the amounts of exchangeable Ca and CaCO_3 determine the P buffering capacity.

2.7.2 Phosphate Diffusion in Soil

Diffusion of phosphorus through the soil to the roots is the dominant mechanism governing the P-uptake by roots growing in all soils, except those extremely high in phosphorus. Barrow (1989) suggested that phosphate mostly moves to plant roots by diffusion and it is only the phosphate in the soil solution that is free to move. The plant root reduces the soil-P mainly by absorbing from the adjacent soil solution, which initiates the diffusion of P in the soil solution towards the plant root and dissolution of solid phase P, termed as the labile pool (Schofield, 1955).

The intensity or the concentration of P in the soil solution is determined by the percent saturation of the P adsorption capacity (Kamprath and Watson, 1980). The replenishment process, which involves the increase of P concentration in soil solution, has been regarded as the primary index of available P (Schofield, 1955; Holford, 1989). At any particular concentration of P, the higher the buffer capacity, the greater the replenishment of P.

The concentration gradient in soil across the root surfaces is an important factor influencing P diffusion (Kamprath and Watson, 1980).

Soil texture is another factor affecting diffusion of P (Olsen and Watanabe, 1963). As the clay content increases, the diffusion coefficients increase due to a decrease in tortuosity and an increase in buffering capacity. The diffusion of phosphate persists until the equilibrium is established. Since the diffusion of phosphorus occurs essentially in the liquid phase and an individual phosphate ion spends a relatively

short time in this phase, the diffusion coefficient of phosphorus in the soil solution will be different from that in free solution.

Diffusion coefficient of phosphate through soil is in the range of 10^{-8} to 10^{-11} cm^2s^{-1} . Diffusion through the soils phase is extremely slow and the phosphate ion, being negatively charged, would not likely diffuse along the negatively charged surfaces of soil particles.

Fitter (1992) stated that a phosphate ion normally moves less than a millimeter through the soil in a day. The diffusion coefficient for phosphate ion in water is $0.89 \times 10^{-5} \text{cm}^2\text{s}^{-1}$. Phosphorus diffusion through soil is slower than in pure water for three reasons, (i) soil water occupies only part of the soil so the cross-sectional area for diffusion is less; (ii) the diffusion path is tortuous because the water is present as films around soil particle; and (iii) most of the diffusible phosphorus is adsorbed on soil surfaces which equilibrate with and buffers the small amount of phosphorus in soil solution.

According to Sibbesen (1983) the P uptake of a plant root over a period of time depends on: the initial concentration of P in soil solution; the soil medium for P-diffusion; and the P dissolution of solid phase P, as a function of decreasing solution P-concentration with time, changing activity of HCO_3^- and H^+ in the rhizosphere, changing activity of exuded organic anions and changing activity of phosphate precipitating cations. All the factors that govern the rate phosphorus diffusion to the root and the extent of root growth are important in determining the availability of phosphorus to growing plants in a soil.

2.8 ADSORPTION AND RELEASE OF PHOSPHATE IN THE SOIL

The main source of plant available P is generally termed the labile pool. This provides fairly rapid exchange with soil solution, maintaining the solution concentration. The remaining fraction is the non-labile pool. This contains a large quantity of insoluble phosphate, which is very slowly released into the labile pool. Various organic and inorganic phosphates constitute these labile and non labile pools. There is no clear distinction by which a particular form can be assigned to labile or non labile pool. In general the labile pool can be considered as orthophosphate adsorbed onto surfaces of clay minerals, hydrous oxides and carbonates plus iron and aluminium phosphates. The relationship between the quantity of phosphorus in the labile pool and the soil solution concentration depends particularly on soil texture and pH (Archer, 1988).

When soluble P compounds are added to the soil, they react rapidly with various soil components and are quickly converted to slowly available forms thus creating one of the main problems relevant to the maintenance and improvement of soil fertility. The reaction between orthophosphate ions and soil has been a subject of considerable study and controversy. However, workers agree that the reactions are complex and generally range from true adsorption to the precipitation without clear delineation between the two mechanisms (Mott, 1970).

Phosphorus fixation is a serious problem in alkaline and calcareous soils (Sharif *et al.*, 2000). The soil can rapidly and firmly adsorb large amounts of P from solution and once adsorbed, they are difficult to release (Huang, 1998). In calcareous soils, the dynamics of P is controlled by many soil properties that strongly retain P and consequently maintain low P concentration in soil solution (Bertrand *et al.*, 1999). The extent of P sorption is relatively higher in fertilized soil and progressively

decreases with increasing rate of fertilizer P in both manured and un-manured soils (Reddy *et al.*, 1999).

In recent years interest in plant available phosphate has centered on, the concentration of phosphate in the soil solution, amount of exchangeable phosphate and the relative rate of adsorption from the soil.

The first two factors are static and can be related to each other by adsorption isotherms. The exchangeable P can be measured by using a suitable technique. Desorption by Olsen's extraction method (0.5 M NaHCO₃ solution) has been well correlated with plant yield in a wide range of soils (Rashid and Rowell, 1988). Ballaux and Peaslee (1975), working on natural soils, proposed a unique characteristic like clay content of the soils may provide an index of the sorption and/or desorption properties for grouping them on the basis of their reaction with added P and its subsequent release

The immediate source of phosphate-P to plant roots is the soil solution. Phosphate deficiency in soil usually occurs from too low concentration of orthophosphate in the soil solution rather than from an inadequate total P content. The concentration of P in the solution is governed by a dynamic equilibrium between solid and solution phases where phosphate is continually released from and re-adsorbed by the solid phase. Any change in the P concentration of soil solution will initiate physico-chemical processes to re-establish the equilibrium.

These processes play a major role in the availability of phosphorus to plants as well as in improving the efficiency in fertilizer use. A decrease in the concentration of P due to plant uptake tends to dissolve and/or desorb P from the solid phase. The opposite processes of P precipitation or adsorption will come into effect when

soluble phosphate fertilizer is added to the soil. Thus the concentration of phosphate in the soil solution at any time is governed both by root uptake and adsorption or release of phosphate by solid phase (Khasawneh, 1971)

Phosphate adsorption is a process in which phosphate ions in solution react with atoms on the surface of soil. The extent, to which this reaction occurs, is an important property affecting both the availability of phosphate to plants and the effectiveness of phosphate fertilizer.

When soluble phosphate compounds are added to the soil they undergo a series of complex reactions. These compounds react rapidly with soil minerals, by precipitation reactions and adsorption onto surfaces, and the availability of this added P declines.

In soils, the problem of differentiating the adsorption from precipitation is made difficult by the fact that new bulk solid phases can precipitate onto surfaces of existing solid phases and that weathering solids may provide host surfaces for the more stable phases into which they transform. The chemistry of these reactions between solids and solution is of fundamental importance in agriculture.

Soil particle surfaces, whether they are of constant or variable charge type, are able to hold ions derived from the soil solution in close proximity to the solid. This acts as a potential store of nutrients able to replenish the soil solution when they are removed by the roots or microbial uptake. To study the phenomenon at the surface, subsamples of a soil are equilibrated at constant temperature with a number of solutions containing different concentrations of phosphate and then the amount remaining in solution after adsorption is determined.

The time of equilibrium varies with the system being studied. A simple cation exchange may be essentially completed within minutes, whereas the adsorption of orthophosphate can continue increasing for two days even after these proceed at a very slow rate for some months (Wild, 1988).

The equilibrium between solid phase and solution phase P is usually expressed by the buffering capacity of a soil in the shape of adsorption isotherm, which is a line showing the relationship between quantity of P adsorbed by the soil and the changing concentration of P in the surrounding solution. According to Holford (1989) the buffering capacity or sorptivity of a soil is controlled by the two fundamental soil properties: one is the extent or number of P-reactive sites, and the other is the affinity of these sites for P.

These processes may be on the soil colloidal surfaces (adsorption) or in the solution (precipitation). Numerical estimates of these properties can be obtained by fitting a suitable equation such as Langmuir or Freundlich equation to the adsorption isotherm. Some parameters of adsorption can be obtained from these equations to compare the behaviour of P in soil.

Phosphorus adsorption is usually measured by shaking samples of soils with solutions containing different concentrations of P in a supporting electrolyte like CaCl_2 for a given time. The P remaining in solution is measured and the amount of P adsorbed is calculated by subtracting the amount remaining in solution from the amount of P initially present.

Many researchers have used 0.01M CaCl_2 solution as the supporting electrolyte (Fox and Kamprath, 1970). The use of 0.01M CaCl_2 solution is based on the assumption

that it approximately represents the ionic strength of solutions in agricultural soils and because it gives a clear solution for analyses.

The adsorption isotherm is the most useful experimental procedure in the study of interaction of anions with oxides or soils and has been used by many workers to measure the adsorption capacity of soils (Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Barrow, 1970, 1978).

The adsorption capacity of soils has been an important criterion in soil classification (Rajan, 1973; Breeuwsma *et al.*, 1986). The adsorption curves provide an adequate basis for estimation of P requirements across a diversity of soils and environment (Van Der Zee *et al.*; 1979). Adsorption isotherms have an advantage over conventional methods of soils testing, because the isotherms encamp both intensity and capacity factors (Rajan, 1973; Tiarks, 1982).

Several factors apart from the nature of the soils used may affect adsorption of phosphate. Barrow (1978) enumerated these as: the period and temperature of contact between soil and phosphate solution, the method of shaking, the P solution: soil ratio; the identity and concentration of the supporting electrolyte used; the moisture content of the soil prior to treatment, and previous addition of phosphate or other specifically adsorbed anions.

2.9 THE ADSORPTION ISOTHERM

Bache (1964), Muljadi *et al.*, (1966) and Olsen and Khasawneh (1980) revealed that the isotherm from a plot of phosphate retained against different equilibrium concentrations could be divided into three regions corresponding to three distinct stages in soil phosphate interaction: (a) The first region corresponding to low

phosphate addition resulting in practically complete adsorption or a negligible fraction of the added phosphate remaining in the equilibrium solution. The adsorption isotherm rises steeply and remains close to the Y-axis; (b) the second region is the strongly curved portion of the isotherm which is convex to the Y-axis. Bache (1964) showed that adsorption in this region varies logarithmically with the equilibrium phosphate concentration; and (c) The third portion of the isotherm approaches linearity and occurs at medium to high phosphate concentrations. Here the adsorption varies linearly with the amount of P in equilibrium in solution. At high level of this region, the slope of line is small and the isotherm, for most soils, tends to become more or less parallel to the X-axis. Freeman and Rowell (1981) have also described the reaction isotherms of phosphate with calcite surfaces in three stages.

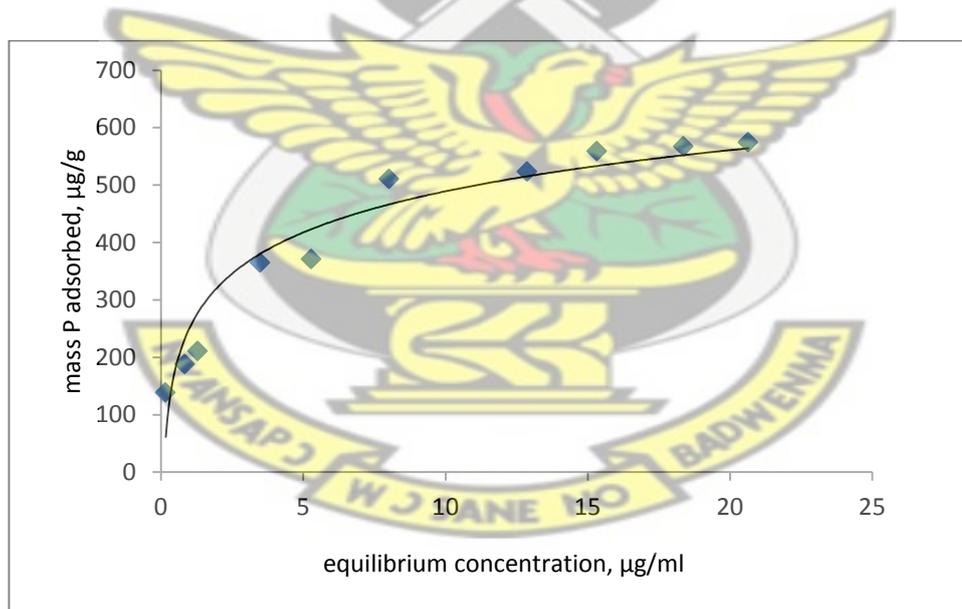


Fig. 1.3 Typical P adsorption isotherm

2.9.1 Types of Adsorption Isotherms

The reaction between phosphate and soils in particular has been described mathematically by several adsorption isotherm equations i.e. Langmuir equation

(Bolster and Hornberger, 2007; Jiao *et al.*, 2007; Jiao *et al.*, 2008), Freundlich equation (Zhang and Selim, 2007; Bolster and Hornberger, 2007; Jiao *et al.*, 2008), Temkin equation (Anghinoni *et al.*, 1996; Ioannou *et al.*, 1998. Ahmed *et al.*, 2008) and Elovich equation (Dimirkou and Ioannou, 1998; Olsen and Watanabe, 1957; Fox and Kamprath, 1970; Juo and Maduakor, 1974; Singholka *et al.*, 1975; Singh and Tabatabai, 1977; Kanabo *et al.*, 1978; Dandy and Morrison, 1980; Lewis *et al.*, 1981; Mead, 1981; Moody and Radcliffe, 1986; Mehadi and Taylor, 1988).

Among these equations the Langmuir and Freundlich equations are the most frequently used to describe the relationship between equilibrium P added and P sorbed by the soils. Sorption parameters derived from these equations may predict the maximum sorption capacity (K_{max}) and abundance of adsorption sites (a) for the soils and are therefore useful in analyzing soil fertility and other management parameters.

2.9.1.1 Langmuir Isotherm

Langmuir equation, proposed by Langmuir in 1916 for adsorption of gases on clean solid surfaces, was first used by Olsen and Watanabe (1957) to describe phosphate adsorption in soils. It is based on the assumption that the energy of adsorption is independent of the surface coverage. In its linear form, the Langmuir equation can be written as:

$$\frac{C}{X} = \frac{1}{Kb} + \frac{C}{b}$$

Where C = equilibrium concentration of phosphate in solution ($\mu\text{g P/ml}$),

X= mass of phosphate adsorbed (μg)/ mass of soil (g)

K = adsorption maximum (mg P/g soil), b is related to the binding energy of soil.

A plot of C/X against C should give a straight line, from which the adsorption maximum K , is the inverse of the slope and the constant b , ($b = \text{slope}/\text{intercept}$) related to energy of adsorption or binding energy can be readily calculated.

Adamson (1960) listed three principal postulates of Langmuir isotherm;

- a. the energy of adsorption is constant, which implies uniform sites and no interaction between adsorbed molecules for the gases but for soil ions were adopted
- b. Adsorption is on localized sites, which implies no translational motion of adsorbed ions in the plane of the surfaces and
- c. The maximum adsorption possible corresponds to a complete mono ionic layer. Larsen (1967) reported that all of these postulates will hold for P in soil.

The use of Langmuir equation appears satisfactory because its derivation is acceptable on theoretical grounds and it contains parameters, which have physico-chemical significance (Olsen and Watanabe, 1957; Holford *et al*, 1974) representing the extensive (adsorption capacity) and intensive (affinity) properties of the adsorbent for the adsorbate (Holford, 1982). However, deviations from the expected linearity have been reported at high phosphate additions (Olsen and Watanabe, 1957; Ryden *et al.*, 1977b).

Langmuir isotherm can often be used to give a measure of the energy by which phosphorus is bonded to the solid and an adsorption maximum. Based on this maximum, calculation of the degree of phosphate saturation can be made, which has

been shown to be related to plant uptake of soil phosphorus (Gunary and Sulton, 1967; Holford and Mattingly, 1976 b).

Holford (1982) reported that the Langmuir equation gave a much useful estimate of affinity (bonding energy) and sorptivity (adsorption maximum) over a concentration range up to 0-5 ug phosphorus mL⁻¹. These adsorption parameters can be utilized in differentiating adsorption properties between soils and characterizing the availability of labile phosphate in soils. The sorptivity parameter is an excellent index of the potential immobility or unavailability of labile phosphate in soils (Holford 1979).

Larsen (1967) and Harter and Baker (1977) have reported that Langmuir plots are most commonly curvilinear. This problem has been resolved by assuming that the theory is obeyed at low equilibrium concentration (Olsen and Watanabe, 1957; Rennie and McKercher, 1959), by resolving the curve into two straight lines and equating to two adsorption mechanisms (Harter, 1968; Syers *et al* 1973; Holford *et al*, 1974).

Gunary (1970) obtained better fits of Langmuir equation by adding a square root term to the equation.

$$1/X = B + \frac{A}{C} + D/\sqrt{C}$$

K_{max} is the inverse of B

C = equilibrium concentration of phosphate in solution (µg P/ml),

X= mass of phosphate adsorbed (µg)/ mass of soil (g)

A, B and D are the Gunary adsorption constants

Rajan and Fox (1975) and Ryden and Syers (1975) have used the two-term Langmuir relationship to obtain improved understanding of the soil phosphate

interaction. Use of the two-term Langmuir equation has been considered appropriate for phosphate adsorption studies since P is retained in soils by surfaces with different affinities for phosphate. The two surface Langmuir equation gives meaningful estimates of phosphate adsorption capacity (Holford *et al.*, 1974) which is greatly under estimated by simple Langmuir equation (Holford, 1982).

In all the models in use the only parameters considered are the equilibrium concentration "C" and the retained phosphate "X" either in the original form or in the modified form by taking into account the phosphate already adsorbed as suggested by Olsen and Watanabe (1957), Bache and William (1971), Fitter and Sulton (1975) and Mendoza *et al.* (1990).

2.9.1.2 Freundlich Isotherm

Freundlich equation was the first model to be used in describing phosphate retention (Russell and Prescott, 1916). Barrow (1978), advocated that the adsorption data from dilute solution could be fitted to Freundlich equation in the following form:

$$X = aC^n$$

Where K and n are empirical parameters, *a* is the sorption energy and *n* the sorption constant.

C is the equilibrium concentration of adsorbate in mg/L and

$$X = \text{mass of adsorbed P } (\mu\text{g})/\text{mass of soil (g)}$$

The equation was originally empirical, without any theoretical physico-chemical foundation, and no significance can be attached to the coefficients (Olsen and Watanabe, 1957; Holford, 1982), (Aslam *et al.*, 2000; Arshad *et al.*, 2000; Javid and Rowell, 2003; Chaudhry *et al.*, 2003).

It implies that energy of adsorption decreases exponentially as the fraction of covered surface increases (amount of adsorption). Freundlich equation can be derived theoretically by assuming that the decrease in energy of the adsorption with the increasing surface coverage is due to surface heterogeneity. Freundlich equation is normally used in its logarithmic form; $\log X = 1/n \log C + \log a$.

A plot of $\log X$ against $\log C$ should give a straight line. Though it is the oldest adsorption equation in the literature on phosphate adsorption, it has been shown to give better fits to adsorption data than the Langmuir isotherm (Gunnary, 1970; Fitter and Sutton, 1975) especially in many soils over limited concentration ranges (Barrow and Shaw, 1975).

Bache and Williams (1971) and Fitter and Sutton (1975) reported that plots of logarithm of adsorbed versus logarithm of concentration gave gentle curves rather than the straight lines required by Freundlich equation. Barrow (1978) described two aspects relevant to this equation; one is that a logarithmic plot involves the transformation of data in which values of low concentration are given a high weighting; the second aspect is the difficulty of taking adequate account of the phosphate already present in the soil and taking part in the equilibration. This problem is common to all equations. However Fitter and Sutton (1975), Barrow (1978) and Torrent (1987) showed that the plot of adsorption data according to Freundlich equation gives straight lines, if correction is made for the phosphate already adsorbed on the surface.

Freundlich relationship has been used only for the theoretical treatment of phosphate adsorption. It has not been possible to compare quantitatively adsorption data for soils obtained from plot of Freundlich equation because the equation was assumed to be empirical (Aslam *et al.*, 2000; Arshed *et al.*, 2000). However, some workers

suggested that the intercept and slope of a linear Freundlich plot could be used to compare phosphate adsorption in soils (Kuo and Lotse, 1974; Holford, 1982). Freundlich equation has also the limitation that it does not predict a maximum adsorption capacity. Despite its limitation the equation was a better fit to phosphate adsorption isotherms in most of the soils than the most widely used Langmuir equation (Fitter and Sutton, 1975) and as good fit as the more complex two -surface Langmuir equation (Barrow, 1978; Sibbesen, 1981)

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2.9.1.3 Temkin Adsorption Equation

$$X/m = a + B \ln C$$

Where $X/m =$, mass of adsorbed P (μg)/mass of soil (g)

C is the equilibrium P concentration ($\mu\text{g/ml}$),

and a and B are parameters.

A plot of X/m against $\ln C$ gives a straight line if the adsorption process fits the model. The values of a and B are obtained from the intercept (a) and the slope (B), respectively. The B value of Temkin equation is considered as the P-buffering capacity (retention capacity of adsorbed P) of soil ($\mu\text{g/g}$), (Anghinoni *et al*, 1996).

2.10 FACTORS AFFECTING P SORPTION FROM SOILS

2.10.1 Soil pH

Soil pH has profound effect on the amount and manner in which soluble phosphates become adsorbed. When soil is acidic, the dominant P ion species present is H_2PO_4^- and when soil becomes alkaline (Higher pH), the dominant ion becomes PO_4^{3-} (Gillian and Sample, 1968). This is represented by the equations below:



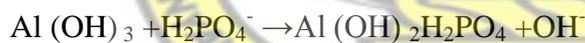


Adsorption of phosphorus by iron and aluminium oxides also declines with increasing pH (White, 1980). Gibbsite ($\text{Al}(\text{OH})_3$) adsorbs greatest amount of phosphate between pH 4 and 5. Phosphorus adsorption by goethite (an- FeOOH) decreases steadily between pH 3 and 12 (Huang, 1975).

Phosphate availability in most soils is at a maximum in the pH range of 6.0 to 6.5 (Tisdale *et al.*, 1985). At lower pH values the retention results from the reaction with iron and aluminium and their hydrous oxides. Above pH 7.0 the ions of calcium, and magnesium and their carbonates cause precipitation of added phosphorus, which decreases its-availability. At pH less than 5.0, there is either the precipitation of P by Fe or Al according to the equation below



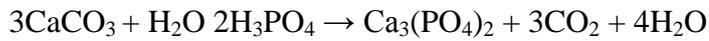
Or sorption by hydroxide of Fe and Al as



2.10.2 Soil Carbonate

Lajtha and Bloomer (1988) regarded calcium carbonate as the primary geochemical agent capable of retaining P in the soils of a desert ecosystem. Tiessen *et al.* (1984) suggested that Ca-bound forms of P constitute the dominant pool of mineral-soil P in arid and semi-arid soils of southwestern United States. The presence of calcium or magnesium ions must accompany high pH values. At pH values above 7.5 the ions

of calcium and magnesium as well as their carbonates cause precipitation of the added P, and their availability decreases. The equation below explains further.



If the increase of these ions (calcium and magnesium) continue, there will be a decrease in solubility of soil phosphorus. However, liming acid soils increase the solubility of phosphorus. In calcareous soils calcium bound phosphate Ca-P is the most important and dominant P fraction (Kuo and Lotse, 1972). The reaction of added phosphate with calcareous soils as CaCO_3 involves initial adsorption of small amounts of phosphate followed by precipitation of high levels of Ca-P. Griffin and Jurinak (1974) showed that P adsorption is actually a three way process in calcareous soils:

- a. Chemisorptions of phosphate associated with heterogeneous nuclei of amorphous Ca-P
- b. Slow transformation of these nuclei into crystalline apatite
- c. Crystal growth of precipitated apatite

However the formation of precipitated Ca-P could be affected by factors such as solution conditions, time of reaction and the nature of adsorbate surface (Freeman and Rowell, 1981)

The phosphorus adsorption on pure CaCO_3 or limestone has been measured by Cole *et al* (1953) who concluded that there are two different types of reactions corresponding to low and high ranges of phosphate concentration. At the lower range of phosphate concentration (9 mg P/ L), adsorption followed the Langmuir model and is directly proportional to the amount of CaCO_3 present. They indicated that at this concentration, there was evidence of precipitation probably of dicalcium

phosphate dihydrate (DCPD). Nearly all the phosphate sorbed at low concentration (in a mono layer) was readily exchangeable with ^{32}P in solution, whereas less than one third of the phosphate adsorbed at higher concentration was isotopically exchangeable indicating precipitation of calcium phosphate compounds at the expense of CaCO_3 which act as a relatively soluble form of Ca^{2+} .

Amer and Ramy (1971) concluded from solubility equilibrium studies that octacalcium phosphate (OCP) rather than DCPD was precipitated when CaCO_3 reacted with KH_2PO_4 and confirmed this by measuring the ratio of surface Ca: surface P by isotopic exchange when the amount of phosphate retained exceeded $44 \mu\text{molg}^{-1}$ of CaCO_3 .

Woodruff and Kamprath (1965) also listed the possible reactions leading to P fixation in calcareous soils to be:

- a. Precipitation of relatively insoluble calcium phosphate such as octacalcium phosphate, hydroxyl apatite and carbonate apatite favoured by high calcium activity and high pHs
- b. Surface precipitation with free calcium carbonate.
- c. Fixation of phosphate by clays saturated with calcium

2.10.3 Ionic Strength of Soil Solution

Both organic and inorganic anions compete with phosphate for adsorption sites to varying extent. In some cases it may result in a decrease in the adsorption of added phosphate or desorption of retained phosphate. Weakly held inorganic anions such as nitrate and chloride are of little significance, whereas specifically adsorbed anions like hydroxyl, sulphate and molybdate are competitive.

The strength of bonding of the anions with the adsorption surface determines the competitive ability of that anion. For example, sulphate, even though considered to be specifically adsorbed anion, is unable to desorb much phosphate (Zhang *et al.*, 1987). Species and concentration of cations in the soil solution also influence the adsorption of P by soils.

Divalent cations enhance P sorption more than monovalent cations (White, 1981). For example clays saturated with Ca^{2+} have the capacity to retain greater amounts of P than those saturated with Na^+ or other monovalent cations. The explanation for this effect of Ca^{2+} involves the making of positive charges edge sites of crystalline clay minerals more accessible to P anions for sorption. On the other hand, both organic and inorganic anions compete to varying degrees for P sorption sites, resulting in some cases, a decrease in the sorption of added P (Moshi *et al.*, 1974)

2.10.4 Organic Matter

Several authors have noted a correlation between organic C and the amount of P adsorbed by soils (Woodruff and Kamprath, 1965; Ahenkorah, 1968). According to Tisdale *et al.* (1985), the availability of phosphorus increased from decomposition of organic residues has been due to:

- a. The formation of phosphohumic complexes which are more easily assimilated by plants
- b. Anion replacement of the phosphate by the humate ions, and
- c. The coating of sesquioxide particles by humus to form a protective cover and thus reduce phosphate retention capacity of the soil.

It was suggested that certain organic anions form stable complexes with iron and aluminum, thus preventing their reaction with phosphorus by blocking the adsorption sites (Leaver and Russell, 1957). It was further stated that these complex ions release phosphate previously retained by the same mechanism. Harter (1969) suggested that it is OH groups in organic matter which affect phosphate adsorption through anion exchange, while the results of Appen *et al*, in 1975 showed that it is the Al and to lesser extent the Fe adsorbed by the organic colloids which are active in P adsorption.

Organic matter does not only lower the adsorption of P, it also provides a method of increasing the P availability without the use of fertilizers. The evolution of carbon dioxide after the decomposition of organic residues has a favorable effect on phosphate availability. The gas is dissolved in water to form carbonic acid, which is capable of decomposing certain primary soil minerals.



On the basis of available evidence, it is clear that the addition of organic materials to mineral soils may increase the availability of soil phosphate.

Organic matter is also an ill defined ion exchanger and has a net negative charge. Organic matter previously sorbed on hydrous oxides block sites on which phosphate could sorb (Moshi *et al.*, 1974; Parfitt, 1990). Presumably the organic matter itself contains available citrate chelates of Al and Fe.

Robert (1969) indicated that P is initially bonded to anion exchange sites on organic matter and subsequently transformed into less soluble Fe and Al phosphate. The organic matter and lime significantly increased pH and extractable P of the acidic

soils increased. Therefore, application of organic matter and lime decreased P adsorption capacity of soil and index of bonding energy of the soil particle for P (Lucrecio and Duque, 1999). The maximum buffering capacity (MBC) was directly correlated with soil organic matter, potential acidity and inversely correlated with base saturation (Guilherme *et al.*, 2000).

There are two principal mechanisms whereby organic matter may affect the captivity and hence availability of phosphorus in soils:

- a. Negatively charged organic matter adsorbs or complexes cations such as Al and Fe in acid soils (Thamos, 1975; Bloom *et al.*, 1979) and Ca in calcareous soils (Barrow, 1973) and hence reduces their solution activities and their role in P sorption and precipitation.
- b. Organic anions compete with phosphorus ions for adsorption sites on P reactive surfaces.

These reactions may be manifested by a decrease in P adsorption capacity (Weir, 1972; Lindsay, 1979) or in high affinity adsorption of P (Weir and Soper, 1962). On the other hand correlation studies often indicate a positive relationship between the organic matter contents of soils and P adsorption (Moreo *et al.*, 1960). This may mean that organic anions and P ions are adsorbed on the same type of sites on colloidal surfaces or P adsorption on Al, Fe or Ca complexes on enlarged organic matter surfaces may cause it. Hence the retention and incorporation of crop residues and green manure crops could, in the long term, have a beneficial effect on P fertility.

Studies to test this hypothesis have shown that, while increasing organic matter did not necessarily decrease sorption capacity, it did increase the availability of native P

in a neutral soil (Weir and Soper, 1963) and of fertilizer P in a very acid soil (Le Mare *et al.*, 1987).

2.10.5 Effect of temperature:

Temperature affects most physical processes and the speed of chemical reactions generally increases with a rise in temperature. Barrow in 1979 described three effects of temperature on phosphate in soil, which are not always distinguished

- a. The position of the equilibrium between phosphate in solution and adsorbed phosphate,
- b. The rate of transfer from adsorbed to firmly-held, and
- c. Rate of transfer from firmly-held to adsorbed phosphate.

If temperature at which phosphate reacts with soil is increased, the rate of reaction is considerably increased (Barrow, 1989). It also has an important theoretical application. As the temperature increases, the kinetic energy of the molecules increase, which enables them to jump over the energy barrier into a new reaction state.

High temperatures are expected to slightly increase the molar solubility of compounds such as apatite, hydroxyapatite, octacalcium phosphate, variscite and strengite. Increase in temperature also stimulates biological activity which enables phosphate to be released from organic residues. Wild, in 1950 estimated that an increase in temperature from 298 K to 308 K increased P adsorption in soils.

The dissolution of water-soluble phosphorus and resultant reactions with soil components to produce less soluble reaction products are hastened by higher

temperatures. There was 33% reduction in concentration of water-soluble phosphorus for each 288 K increase in temperature (Tisdale *et al.*, 1985).

The soils of the warm regions of the world generally adsorb more phosphates than the soils of temperate regions. These warmer climates also give rise to soils with higher contents of the hydrous oxides of iron and aluminum. Many workers agreed that phosphorus retention increases at higher temperatures (Muljadi *et al.*, 1966; Kuo and Lotse, 1974; White and Taylor, 1977).

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2.10.6 Effect of Time

Phosphorus adsorption by soils and many soil components follow two distinct patterns: an initial fast reaction followed by a very much slow reaction. The adsorption reaction involving exchange of phosphate for anions and ligands on the surface of iron and aluminum oxides are extremely rapid (White, 1980; Tisdale *et al.*, 1985). The slower continuing adsorption reactions may involve such changes as:

- a. Diffusive penetration or chemisorptions of surface-adsorbed phosphorus into soil constituents, e.g. the incorporation of phosphorus into hydroxy aluminum or iron polymers and occlusion of phosphorus in the surface of calcite as suggested by Griffin and Jurinak (1973).
- b. The precipitation of a phosphorus compound for which the solubility product has been exceeded (Veitli and Sposito, 1977).

These slow reactions involve a shift in the form of phosphorus held at the surface from more loosely bound to more tightly bound types which are less accessible to plants.

An important practical aspect of time is the period after application of fertilizer. On some soils with high adsorption capacity, the period of reaction is short, whereas on others the period may last for months or even years. The reaction of phosphate with soils can probably never be considered entirely complete as long as an appreciable concentration of phosphate remains in solution.

2.10.7 Clay Mineralogy

Several workers have reported a significant correlation between clay content and P sorption parameters (Fox and Kamprath, 1970; Jones *et al*, 1979; Ayodele, 1981, Morais *et al*, 1996; Sharif *et al*, 2000; Chaudery *et al* 2003). The clay content of a soil has great impact on phosphate adsorption. Soils containing large quantities of clay will adsorb more phosphate than those with less clay content.

Clays, particularly those of 1:1 lattice tend to adsorb more P in tropical soils (especially at low pH) than those of 1:2 lattice, for example soils high in kaolinite such as those found in areas of high rainfall and high temperature, will retain larger quantities of phosphate than those containing the 2:1 types. Greater adsorption of phosphate in the former case is probably due to the higher amounts of hydrated oxides of iron, manganese and aluminum associated with the kaolinitic clays and other 1:1 type clay minerals (Hayne, 1983). In other words, the more a surface area is exposed with a given type of clay, the greater the tendency to retain phosphates.

Additionally, kaolinite develops pH-dependent charges on its edges which can enter into adsorption reactions with phosphate. Clays such as kaolinite with a low $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio will adsorb larger quantity of phosphorus than the clays with a higher ratio. A large number of exposed hydroxyl groups in the gibbsite layer of kaolinite are exchangeable with phosphate and cause more adsorption.

2.10.8 Free Iron and Aluminum

Researchers have long recognized that oxides and hydroxides of Al and Fe play a significant role on P availability and sorption properties. Singh and Singpuri (1986) reported that oxides of Fe and Al were correlated significantly with P adsorption maxima. The higher value of P adsorption maxima in cases of soil containing higher content of oxides of Fe and Al might be due to formation of their respective metal phosphate (Maida, 1980).

A significant and positive relationship between P bonding energy content and free oxides of Fe and Al was observed and suggested a mechanism of phosphate adsorption by two point attachments mainly through the colloidal surface and Al. The sorption of inorganic phosphate of soils with pH less than 7.0 is closely related to the amount of reactive Fe and Al compounds (Syers *et al.*, 1977).

It has been shown that the amorphous hydrous metal oxides of Fe and Al sorb relatively greater amounts of P than their crystalline counterparts (McLaughlin *et al.*, 1981). Syers *et al.*, (1977) reported that phosphate sorption reduced remarkably when oxides of Al and Fe were extracted from the soil. In addition, Tisdale *et al* in 1990 also showed that about 1 meq exchangeable Al per 100 gramme soil when completely hydrolyzed can sorb up to 102 mg P /L in soil solution.

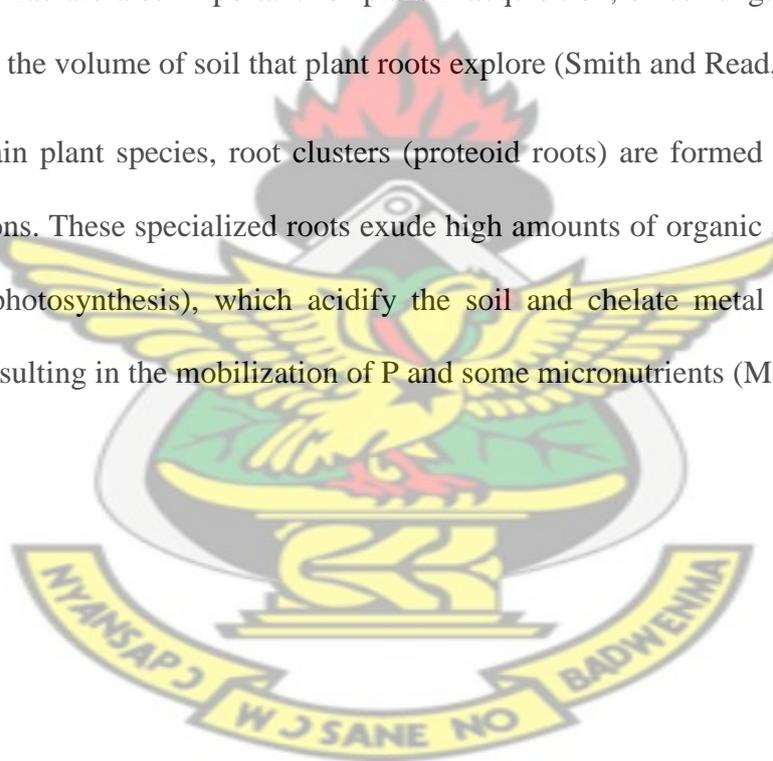
With respect to the relative importance of the two elements, Al plays a dominant role in P retention than Fe (Bromfield, 1965, Williams *et al.*, 1958). Owusu-Bennoah and Acquaye in 1989 also showed that dithionate-extractable Al was a more important determinant of P sorption maxima of some selected Ghanaian soils. Conversely Ahenkorah in 1968 observed no significant relationship between P retention capacity and extractable Al but rather he indicated that dithionite-extractable Fe was responsible for P sorption in some cocoa growing soils of Ghana.

The sorption of P on to Al / Fe surface is usually considered to be important under acidic conditions

2.10.9 Plant Root Geometry

Phosphate uptake is more dependent on plant root activity than is the case for other major nutrients. Plant root geometry and morphology are important for maximizing P uptake, because root systems that have higher ratios of surface area to volume will more effectively explore a larger volume of soil (Lynch, 1995). For this reason mycorrhizae are also important for plant P acquisition, since fungal hyphae greatly increase the volume of soil that plant roots explore (Smith and Read, 1997).

In certain plant species, root clusters (proteoid roots) are formed in response to P limitations. These specialized roots exude high amounts of organic acids (up to 23% of net photosynthesis), which acidify the soil and chelate metal ions around the roots, resulting in the mobilization of P and some micronutrients (Marschner, 1995).



CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Cleaning of glassware

All glassware was washed well with water and soaked overnight in 5% HCl. They were then rinsed with distilled water and dried.

3.2 Apparatus, Glassware and Equipment

25 mL , 50 mL , 100 mL, 500 mL, 1 L and 2 L volumetric flasks

500 mL measuring cylinder

2 mm sieve

Whatman No. 41 filter paper

50 mL centrifuge tubes

ICP- OES (Inductively Coupled Plasma)-Optical Emission Spectrometer

UV-Visible spectrophotometer (Shimadzu UV mini 1240 series)

pH meter

Conductivity meter

3.3 REAGENTS

3.3.1 Phosphorus determination

5 M sulphuric acid (H_2SO_4) was prepared by adding 141 mL of concentrated H_2SO_4 to 800 mL distilled water. The mixture was cooled to room temperature and diluted to 1000 mL with distilled water.

100 mg/L standard phosphate solution: 0.8788 g oven-dried KH_2PO_4 was weighed into 2 L volumetric flasks and 500 mL distilled H_2O was added to

dissolve the salt. The solution was diluted to 2 L with distilled water. Two drops of toluene were added to inhibit microbial activity.

2 mg/L working phosphate solution was prepared by diluting 2 mL of the 100 mg/L standard working solution to 100 mL with distilled water.

0.01 M CaCl_2 solution was prepared by weighing 2.9418 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ into a 2 L volumetric flask and diluting to the mark with distilled water

Reagent A: 12.0 g of ammonium paramolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), was dissolved in 250 mL distilled water. A 0.2908 g of potassium antimony tartarate ($\text{KSb} \cdot \text{C}_4\text{H}_4\text{O}_6$) was dissolved in 100 mL distilled water. The dissolved reagents were added to 1L 5M H_2SO_4 , mixed thoroughly and diluted with distilled water to 2 L. The solution was stored in a Winchester bottle in a dark and cool compartment.

Reagent B: 1.056 g of ascorbic acid was dissolved in 200 mL of reagent A. Only the required amount of this solution was prepared each day because the solution cannot be kept for more than 24 hours.

3.3.2 Reagents for total Phosphorus determination

- 60% Perchloric acid (HClO_4)
- Ammonium paramolybdate-vanadate. Solution was prepared by dissolving 25 g of ammonium paramolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) in 400 mL distilled water. Ammonium metavanadate (NH_4VO_3) was dissolved in 300 mL boiling distilled water. The vanadate solution was cooled to room temperature and 250 mL concentrated HNO_3 was added. The NH_4VO_3 - HNO_3 solution was

cooled to room temperature and the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ solution added. The mixture was then diluted to 1 L with distilled water.

- 100 mg/L Standard phosphate solution.
- Sodium hydrogen sulfite (NaHSO_3). Solution was prepared by dissolving 5.2 g of reagent grade NaHSO_3 in 100 mL of 0.5 M H_2SO_4 .

3.3.3 Reagents for % Organic Matter Determination

- 0.0167 M Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): 49.13 g of $\text{K}_2\text{Cr}_2\text{O}_7$ (previously dried at 102°C for 24 hrs) was dissolved in 500 mL distilled water, 167 mL concentrated H_2SO_4 was added followed by 33.3 g of mercuric sulphate, it was then cooled and transferred into a 1 L volumetric flask and diluted to the mark.
- 0.1 M ferrous ammonium sulphate (FAS), $(\text{Fe}(\text{NH}_4)_2(\text{SO}_4) \cdot 6\text{H}_2\text{O})$: 39.2 grams of the salt was dissolved in distilled water and 20 mL concentrated H_2SO_4 was added, cooled and diluted to the mark in a 1 L volumetric flask. The Fe^{2+} in this solution oxidizes slowly on exposure to air so it was standardized against the dichromate solution daily.

The FAS solution was standardized daily against the $\text{K}_2\text{Cr}_2\text{O}_7$ as follows:

5 mL distilled water was pipetted into a conical flask and 3 mL of dichromate solution was added followed by 7 mL concentrated H_2SO_4 . The mixture was cooled to room temperature and titrated with the FAS solution to a light

green end point using two to three drops of N-phenylanthranilic acid indicator.

Molarity of FAS= (Vol. of $K_2Cr_4O_7$, mL /Vol. of FAS used) *0.1

3.4 SOIL SAMPLING

A total of 12 soil samples from four land utilizations sites in the Eastern Region of Ghana were used in the study. An uncultivated virgin land at Huhunya (HV), a cocoa farm in Akwadum (AC), a plantain farm also in Huhunya (HP) and piece of land which had been allowed to go fallow in Huhunya (HF) were the four sampling sites used for this research. Three soil depths comprising topsoil (0-10cm), a subsurface soil of 10-20cm and a subsoil of 20-30 cm were taken from each site. The soil samples were air dried and passed through a 2 mm sieve prior to analyses. Table 3.1 below shows the representation of the soil samples at the various depths.

Table 3.1 Samples and their code names

Depth (cm)	Akwadum Cocoa farm	Huhunya Virgin land	Huhunya Plantain farm	Huhunya fallow land
0-10 (Top surface)	AC1	HV1	HP1	HF1
10-20 (Sub surface)	AC2	HV2	HP2	HF2
20-30 (Surface)	AC3	HV3	HP3	HF3

3.5 CHEMICAL ANALYSIS OF SOILS

3.5.1 Soil pH

Soil pH was determined using a 1:2.5 (w/v) soil: distilled water ratio using a pH meter.

3.5.2 Soil Conductivity

Soil conductivity was determined using a 1:2.5 (w/v) soil: distilled water ratio using a conductivity meter.

3.5.3 Organic carbon determination

Organic carbon was determined by the wet oxidation method of Walkley and Black (1934). Five mL of $K_2Cr_2O_7$ and 2.5 mL of concentrated H_2SO_4 were added to 0.5 g of soil in a conical flask. The mixture was gently swirled. Excessive swirling that could have resulted in organic particles adhering to the sides of the flask, bringing them out of the solution was avoided. The mixture was then digested on a preheated hot plate at $150\text{ }^\circ\text{C}$ for 30 minutes to ensure complete oxidation. The digest was then cooled to room temperature and diluted to 50 mL with distilled water. It was then titrated against FAS (ferrous ammonium sulphate) solution to a light green end point using 2-3 drops of N-phenylanthranilic acid indicator.

Reagent blank was ran using the same procedure without any soil sample.

Percent Organic carbon was calculated using the formula:

$$\%C = ((B-S) \times M \text{ of } Fe^{2+} \text{ used} \times 12 \times 100) / (\text{g of soil} \times 4000)$$

Where:

B = Volume of Fe^{2+} solution (in mL) used to titrate blank.

S = Volume of Fe^{2+} solution (in mL) used to titrate sample.

$12/4000$ = milliequivalent weight of C in g.

$$\% \text{ Organic Matter} = (\% \text{ total C} \times 1.72) / 0.58$$

3.5.4 Ca, Fe and Al Determination

Exactly 0.5 g soil sample was weighed into a 50 mL Pyrex digestion tube and one mL distilled water, 3 mL concentrated H_2SO_4 and 5 mL of a solution of HNO_3 and HClO_4 in the ratio (1:1) were added. The digestion tube was heated on a preheated hot plate at 200°C for 30 minutes to remove all the organic components. The digest was cooled to room temperature, diluted to the 50 mL mark and filtered into amber bottles for analysis.

A blank solution was prepared in the same manner without any soil. Metals in the soil digests were analyzed using the inductively coupled plasma (ICP) - Optical Emission Spectrometer.

3.5.5 Total P Determination

Total phosphorus was determined by the digestion method of Olsen and Sommers (1982). Two grams of finely ground soil ($<0.5\text{mm}$) was mixed with 30 mL of 60% HClO_4 in a 100 mL digestion tube. The soil and acid mixture was digested at a few degrees below the boiling point on a hot plate in a perchloric hood until the dark colour from organic matter disappeared. Heating was continued at the boiling temperature for at least 20 minutes until heavy white fumes appeared and the insoluble material became like white sand. One to two millilitres of HClO_4 was used to wash down the black particles that stuck to the side of the digestion tube. Total digestion time was approximately 40 minutes. The digest was then cooled to room temperature, diluted to the 100 mL mark with distilled water and filtered into amber bottles for analysis.

To analyze for total P, suitable aliquots of the digest were transferred into 50 mL volumetric flasks. Ten millilitres of the ammonium paramolybdatevanadate reagent

was added and diluted to the mark with distilled water. The absorbances were read after 10 min at a wavelength of 490 nm. A calibration curve was obtained by taking 0 mL, 4 mL, 6 mL, 8 mL, 10 mL and 12 mL of the 2 mg/L standard P solution into 50 mL volumetric flasks, 10 mL of ammonium paramolybdatevanadate reagent was added to each flask and diluted to the mark with distilled water. The absorbances were read at the wavelength of 490 nm. The concentrations of P were then extrapolated from the calibration curve.

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3.5.6 Particle Size Determination

The particle size of the soil samples was determined by weighing exactly 51.0 g of soil sample into a 'milkshake' mix cup. Fifty millilitres of 10% sodium hexametaphosphate and 100 mL distilled water was added. The mixture was shaken for 15 minutes after which the suspension was transferred from the cup into a 1L measuring cylinder. A soil hydrometer was placed inside the suspension and distilled water was added to the 1L mark. The mixture was inverted several times until all soil was in suspension. The cylinder was placed on a flat surface and the time noted. The soil hydrometer was inserted immediately into the suspension and the first reading on the hydrometer taken at 40 seconds. The temperature of the suspension was also taken with a thermometer. After the first reading, the suspension was allowed to stand for 3 hours and the second hydrometer and temperature readings were taken.

Calculations:

$$\% \text{ Sand} = 100 - [H1 + 0.2 (T1 - 20) - 2] \times 2$$

$$\% \text{ Clay} = [H2 + 0.2(T2 - 20) - 2] \times 2$$

$$\% \text{ Silt} = 100 - (\% \text{ sand} + \text{clay})$$

Where:

H = Hydrometer readings at 40 seconds

T1 = Temperature at 40 seconds

T2 = Temperature at 3 hours

H2 = Hydrometer readings at 3 hours

$0.2(T - 20)$ = Temperature correction to be added to hydrometer reading

- 2.0 = Salt correction to be added to hydrometer reading.

Temperature correction is made because the hydrometer is calibrated at 20 °C to read 1.00 in distilled water and variations from this standard temperature produce inaccuracies. Salt correction is also done because the dispersing agent or the salt used (sodium hexametaphosphate) causes an increase in the specific gravity of the readings. This increase must be determined to correct the readings.

3.6 Determination of Equilibrium Period

In sorption studies, it is very important to equilibrate the adsorbent and adsorbate long enough to ensure that a steady state has been reached. However, one should be careful that the equilibrium process is not so lengthy that precipitation or dissolution reactions occur (Sposito, 1984). Additionally, the degree of agitation used in the equilibration process should be forceful enough to effect good mixing but not so vigorous that adsorbent modification would occur (Spark, 1989). For this study, to obtain the optimum equilibration period, one of the samples was chosen and 2 g each was weighed into thirty 50 mL centrifuge tubes and 30 mL of a standard P solution added to each of the centrifuge tubes. The tubes were then shaken for 30 hrs. After

every hour, one of the tubes was taken and the equilibrium P was determined in the supernatant from which P adsorbed was calculated. The time at which there was maximum P adsorption was assumed to be the optimum equilibration period.

3.7 Sorbed P Determination

P solutions (5, 8, 10, 15, 20, 25, 30, 35, 40 and 45 mg P/L) were prepared by diluting the appropriate amount of the already prepared 100 mg P/L standard solution in 0.01 M calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) solution. Two gram samples of each soil was weighed into 50 mL centrifuge tubes in triplicates and 30 mL aliquots of the solutions were added to the centrifuge tubes to obtain 150, 240, 300, 600, 750, 900, 1200, and 1350 μg of added P g^{-1} of soil.

The samples were then shaken for 24 hrs (the optimum equilibration period) at room temperature on an end to end shaker. The suspensions were centrifuged at 5000 rpm (Kontron Instruments, Model CentrikonT-42K) for 10 minutes and then filtered through Whatman No. 41 filter paper. Aliquots of the clear filtrates were analyzed for P remaining in the solution using the molybdenum blue method of Murphy and Riley (1962).

The blue colour was developed by adding 8 mL of reagent B to the suitable aliquots in 50 mL volumetric flasks and diluting to the mark. The intensity of the colour was read using a spectrophotometer at a wavelength of 880 nm.

A calibration curve was obtained by taking 0 mL, 4 mL, 6 mL, 8 mL, 10 mL and 12 mL of 2 mg/L standard P solution into 25 mL volumetric flasks, 4 mL of reagent B was added to each flask and diluted to the mark with distilled water. The

absorbances were read at the wavelength of 880 nm. The concentrations of P were then extrapolated from the calibration curve.

The amount of P adsorbed per gram of soil which is the P that disappeared from the solution was calculated as the difference between the P added to the soils and the P remaining in the solution.

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CHAPTER FOUR

4. RESULTS AND DISCUSSION

A total of 12 soil samples from four land utilizations sites in the Eastern Region of Ghana were used in the study. An uncultivated virgin land at Huhunya (HV), a cocoa farm in Akwadum (AC), a plantain farm also in Huhunya (HP) and a piece of land which had been allowed to go fallow for about ten years in Huhunya (HF) were the four sampling sites used for this research. The soils chosen were of different utilization types. Three soil depths comprising topsoil (0-10cm), a subsurface soil of 10-20cm and a subsoil of 20-30cm were taken from each site.

Summary of results of physical and chemical properties of the soil i.e. soil pH, conductivity, soil organic matter (OM), particle size distribution, the amounts of calcium (Ca), aluminum (Al) and iron (Fe) in mg/kg, the total phosphorus (mg/kg) in the soil and the soil texture are presented in Table 4.1

The pH of the soils ranged from slightly neutral to acidic. Soils from the virgin land in Huhunya (HV) recorded the least pH range of 5.54 to 6.21. The highest pH was recorded by soil from Akwadum (AC). Percentage organic matter for all the soils too was quite low (1.59% - 2.86%).

Table 4.1: Physical and chemical characteristics of soils used for the study.

Sample	Depth (cm)	pH	Cond mS/cm	Organic Matter (%)	Sand (%)	Silt (%)	Clay (%)	Fe mg/kg	Ca mg/kg	Al mg/kg	Total P mg/kg	Soil Texture
	0-10	6.7	0.141	2.392	69.100	8.350	22.550	27.457	3.110	62.113	31.818	Sandy clay loam
AC	10 - 20	6.5	0.109	1.951	75.075	4.875	20.125	28.071	2.105	65.799	28.584	Sandy clay loam
	20 - 30	6.6	0.093	1.936	72.525	4.475	23.000	34.789	2.395	83.746	26.697	Sandy loam
	0-10	5.8	0.103	2.865	84.300	2.000	7.800	15.753	1.635	41.219	22.271	Loamy sand
HV	10 - 20	5.6	0.055	2.753	90.200	7.900	7.800	19.729	1.705	54.981	18.975	Loamy sand
	20 - 30	6.2	0.052	2.562	86.300	7.800	5.900	18.458	1.852	50.885	18.116	Loamy sand
	0- 10	5.9	0.111	2.371	83.633	9.167	7.200	13.438	1.445	28.854	13.897	sandy loamy
HF	10 - 20	5.8	0.063	2.023	81.700	9.167	9.133	10.658	0.804	14.275	12.719	sandy loamy
	20 - 30	7.8	0.050	1.824	82.333	6.567	11.100	14.780	1.192	34.160	12.318	sandy loamy
	0-10	6.7	0.108	2.229	82.375	13.225	4.400	12.550	1.482	19.170	13.081	Loamy sand
HP	10 - 20	6.4	0.072	1.859	83.850	11.725	4.425	12.409	0.953	17.700	11.596	Loamy sand
	20 - 30	6.0	0.045	1.695	84.800	9.800	4.900	12.138	0.894	19.306	12.531	Loamy sand

4.1 Sorption of Phosphorus

Apart from a few contradictory studies (Koss and Kim, 1990), sorption is often observed to increase with the solute concentration. The main reasons proposed for this phenomenon called “solid effect” are (i) the occupied volume of the suspended particles (Celorie *et al.*, 1989) and (ii) their aggregation (Voice *et al.*, 1983; Di Toro *et al.*, 1986) that would prevent an optimal sorption of the solutes. It has been found by Koss and Kim in 1990 that the ratio of solid mass versus solution volume should theoretically not influence the proportion of adsorbed compound. Most of the time, this parameter does not effectively influence the shape of the isotherm if it remains in the same order of magnitude).

The soil samples were equilibrated for 30 hrs on an end to end shaker and P adsorbed was obtained after every one hour. Adsorption of P was rapid for the first few hours but slowed down with time. This is shown in Fig 4.1. Sorption experiments were therefore performed using 24 hours as equilibration period.

The results of this study corroborate the observations that the amount of phosphorus (P) sorbed increased with increase in the concentration of P solutions used.

There was a variation in the amounts of phosphorus adsorbed by the soils. Soils sorbed between 34 % and 48 % of the added P when using 49.17 – 574.26 μPg^{-1} soil as the initial concentration. Soils from site HV2 (10-20cm) sorbed the most P (138.31-574.26 $\mu\text{g/g}$). Soil from HP sorbed the least P from solution at all depths. The various amounts of P adsorbed by the soils at different depths are presented in Table 4.2.

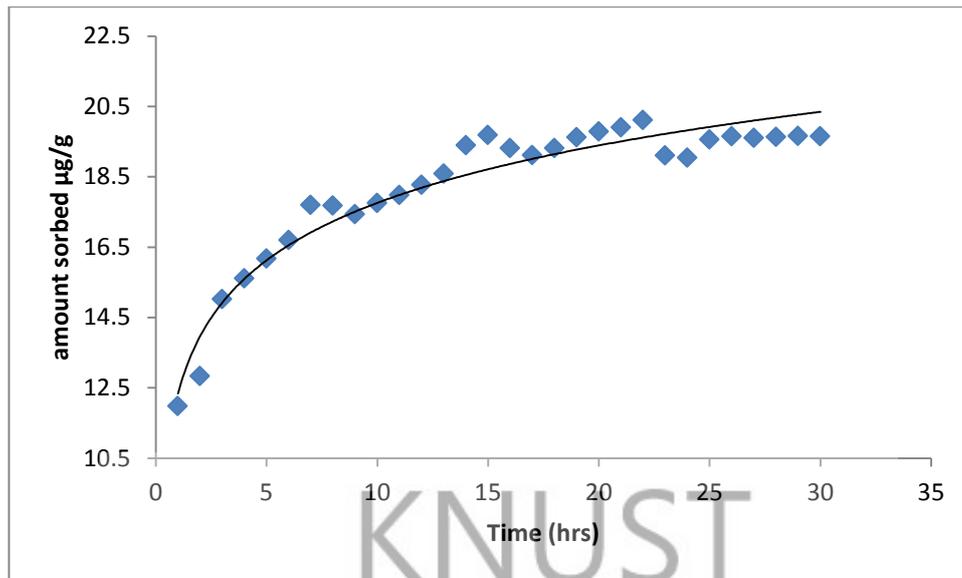


Fig 4.1 Equilibration curve

Table 4.2: Amount of Phosphorus sorbed at various depths.

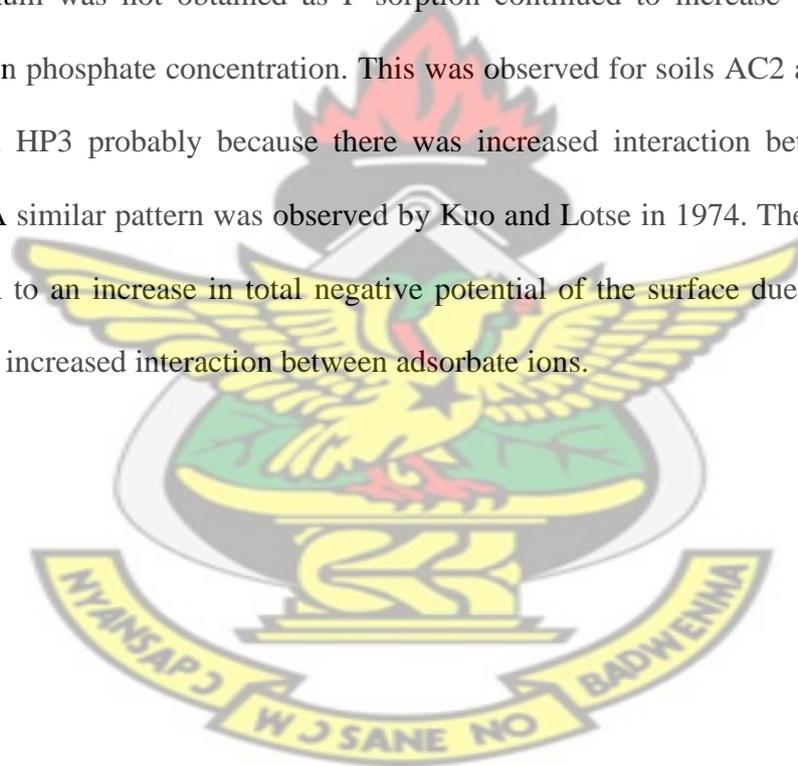
Depth	Amount Sorbed µg/g			
	AC	HF	HV	HP
Suface				
(0 - 10 cm)	95.53-207.2	61.19-154.59	113.04-205.78	49.17-100.61
Sub surface				
(10 - 20 cm)	96.47-196.24	72.81-173.72	138.31-574.26	53.06-125.67
Sub soil				
(30 - 40 cm)	114.16-211.55	74.48-185.25	115.78-204.57	58.84-104.19

4.2 DESCRIPTION OF SORPTION ISOTHERMS

Phosphorus sorption is quantified successfully with P sorption isotherms (Richardson, 1985). These are graphical tools used to characterize the ability of soils to remove inorganic P from soil solution (Richardson, 1985), and help in visual comparison of P sorption relationship as a function of soil properties (Olsen and Watanabe, 1957; Pant and Reddy, 2001).

Phosphorus sorption isotherms relating the equilibrium P concentration of the soils studied to P sorbed are presented in Figures 4.2, 4.3, 4.4 and 4.5. The sorption curves of all the soils were similar indicating similarity in the nature of adsorption reaction, but differed in the intrinsic characteristics such as the slopes of the isotherms and adsorption capacity. This probably resulted from the differences in the amount of P sorbed at a particular P concentration.

For this study, curves obtained from the plot flatten and appear to approach a maximum at higher concentrations. However, in some cases, a well-defined maximum was not obtained as P sorption continued to increase with increase in solution phosphate concentration. This was observed for soils AC2 and AC3 as well as soil HP3 probably because there was increased interaction between adsorbate ions. A similar pattern was observed by Kuo and Lotse in 1974. They attributed this pattern to an increase in total negative potential of the surface due to P adsorption and an increased interaction between adsorbate ions.



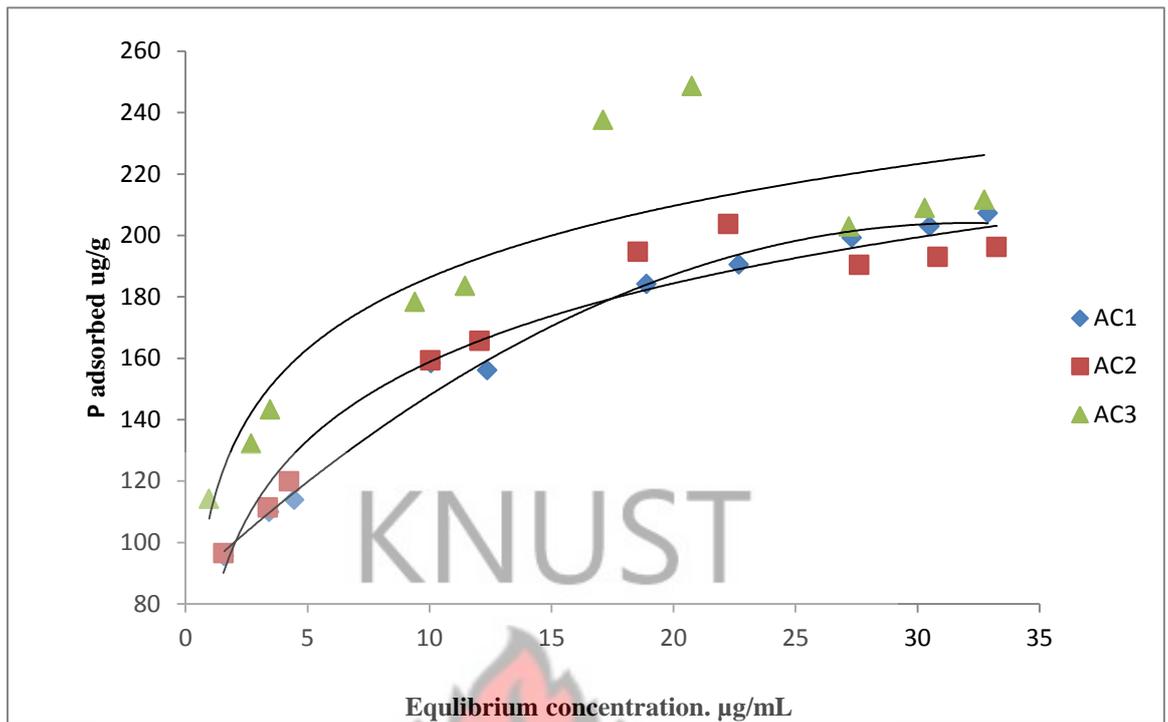


Fig 4.2 Sorption isotherm for soil AC.

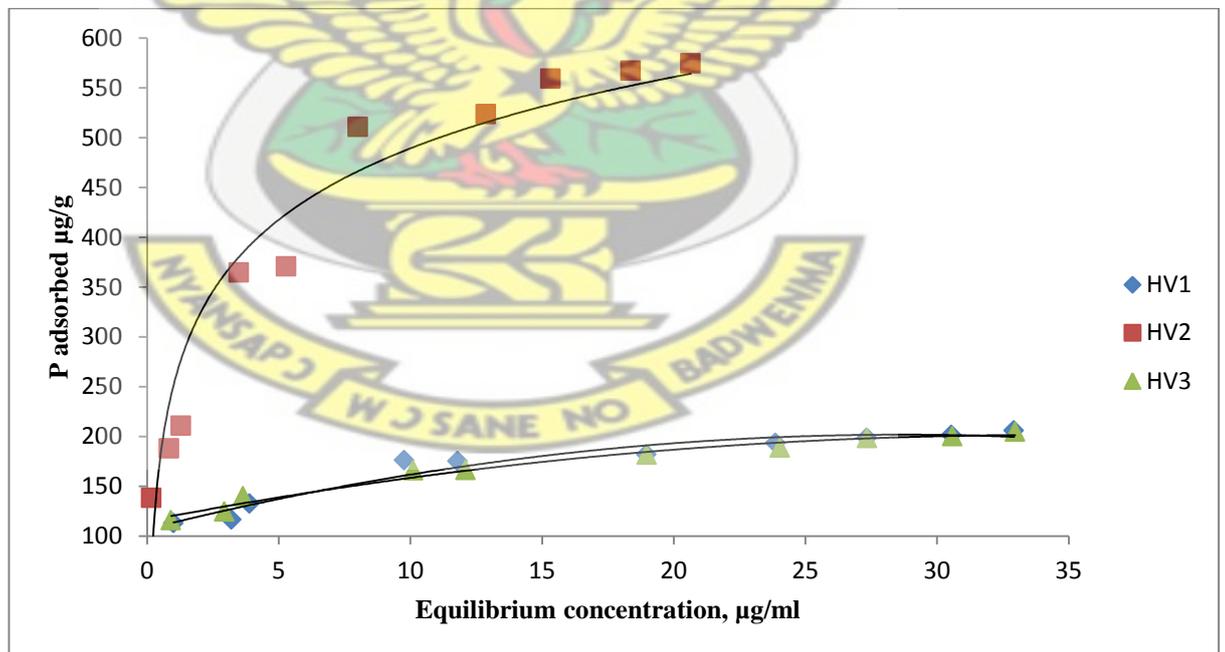


Fig 4.3: Sorption isotherm for soil HV

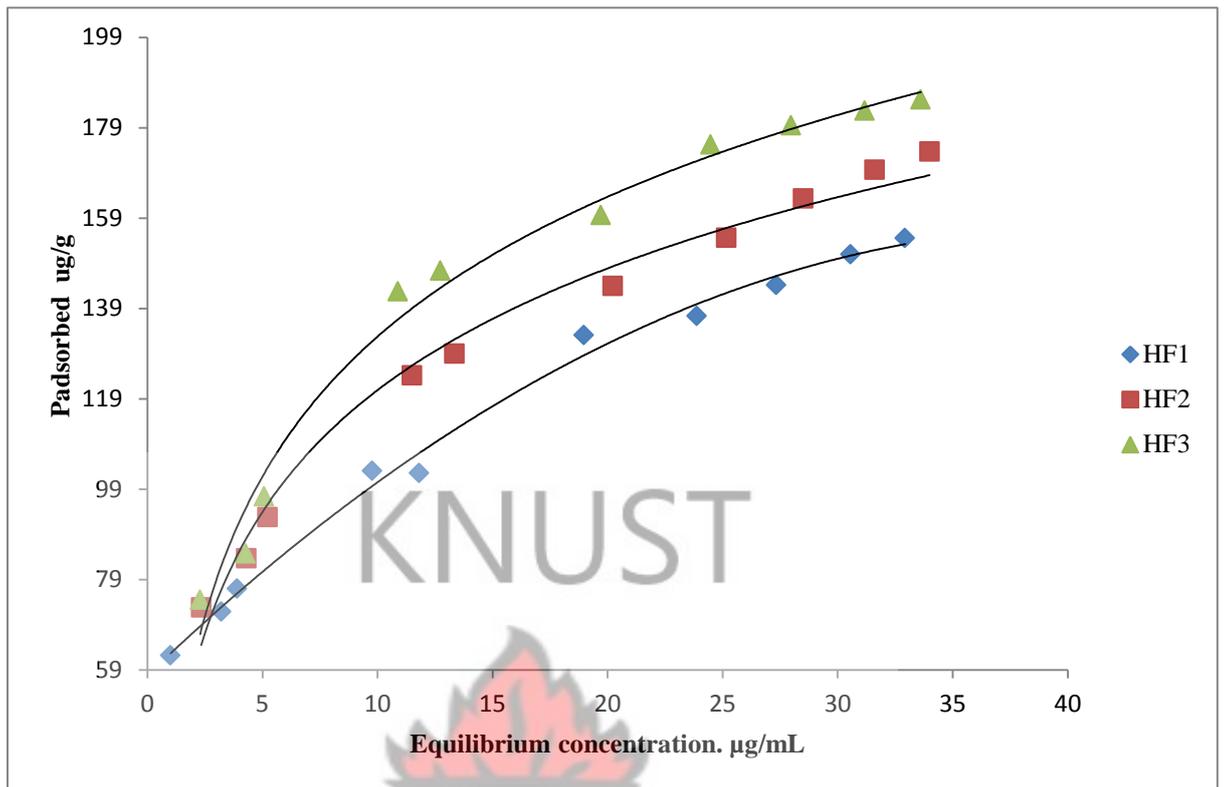


Fig 4.4: Sorption Isotherm for soil HF

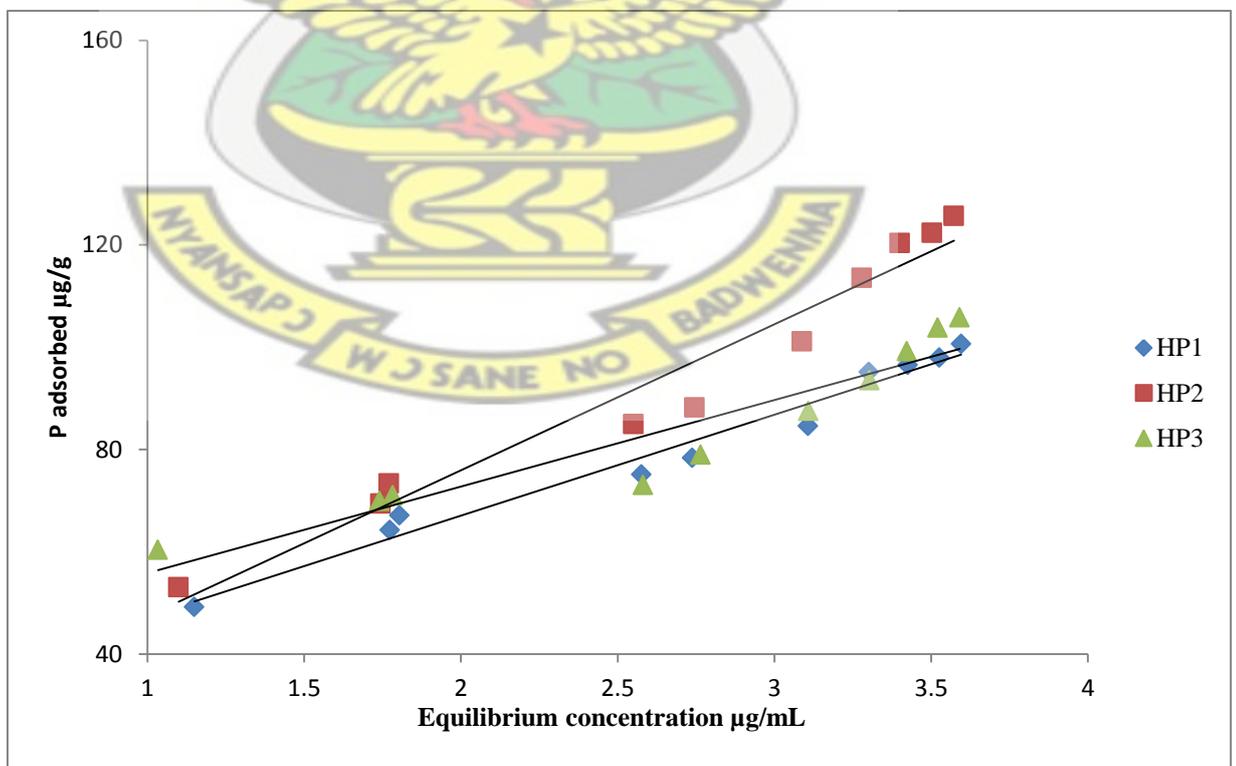


Fig 4.5: Sorption Isotherm for soil HP

The curves obtained for soil from Akwadum (AC) at the three different depths were a bit steep, and were of similar shape, which could be as a result of the similar physical and chemical properties of the soils (Table 4.1). Soil HV which is the Huhunya virgin land, showed two very distinctive isotherm shapes, a very steep isotherm was obtained for the soil depth 10-20 cm i.e. HV2, and gentle slopes were obtained for the other depths. This can be attributed to the larger amounts of aluminum and calcium found in HV2 (Table 4.1). Of all the soils used HV recorded the largest P sorption capacity. At high P sorption conditions, solution P concentration becomes low, and the soil is more likely to be P deficient.

Sorption isotherms developed for Soil HF in Huhunya, exhibited three isotherms which were quite similar in shape. Soil HP, which is from a plantain farm in Huhunya, adsorbed the least phosphorus in solution. Soils obtained from the three depths recorded the highest equilibrium concentrations at all levels of added P. Consequently their isotherms were the least steep of the soils studied Fig (4.5). The main cause of this could be the low amounts of Ca, Al and Fe recorded by this soil. It also recorded a relatively higher pH than the other soils. From Table 4.1, soil HP contained more silt and low clay (loamy sand soils). Such soils because of their coarse texture adsorb low P.

Equilibrium P concentration values indicate the extent of P loading onto soils, i.e. increases in these values reflect increases in P loading. Soils with larger equilibrium P concentration values would be expected to release P into runoff waters. Adsorption was also very even for the soils at the various depths. This could be as a result of the very similar values obtained for their physical and chemical properties (Table 4.1).

Phosphorus retention by soils is generally influenced by soil properties such as clay content, amounts of free Al and Fe oxides, pH, the ionic strength of the solution, organic matter and the mineralogy of the soil (White, 1981).

From this study, the curves obtained for soil AC at three different depths indicate that the soils have a high P adsorption capacity. This could be the result of the large amounts of Fe, Al and Ca contained in the soil and the large amount of clay content. Soils containing large amounts of clay are called clayey soils. Clayey soils are usually able to retain more P because they have high exposed surface areas. There are two schools of thought concerning the effect of clay on P sorption. One school (Ryan *et al.*, 1985; Boreo *et al.*, 1988; Pena and Torrent 1990; Lines and Cox, 1989) have postulated that the larger the amount or quantity of clay, the larger the extent of P sorption. The other school (El-Swaify *et al.*, 1985) also claimed that it is not the amount of clay present but rather the type of clay present that affects P sorption. They suggested that clays such as kaolinite with a low $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio (1:1 lattices) will adsorb larger quantity of phosphorus than the clays with a higher ratio. The results of this study in a way support both schools of thought. For instance, soil AC's clay content was larger than that of HV, but HV retained the most P at all levels. This implies that HV was of a clay type that enhanced P sorption in soils. This supports the observation made by El-Swaify *et al.* 1985. On the other hand, soil AC contained more clay and also adsorbed more P than soils HP and HF. In this case Pena and Torrent's school of thought seems to be supported. Greater adsorption of P in soils with higher clay contents is also probably due to the amounts of hydrated oxides of iron, magnesium and aluminium.

The role of amorphous Fe and Al oxides on P sorption has been well documented. Active amorphous Al, on a per mole basis, adsorbs nearly twice as much P as active

amorphous Fe (Borggaard *et al.*, 1990; Darke and Walbridge, 2000). Borggaard *et al.* (1990) and Freese *et al.* (1992) found that amorphous forms of both Fe and Al were important predictors of soil P-sorption capacity in clayey, peaty, and sandy soils.

From Table 4.1 it can be observed that for this study, although soil AC contained the largest amounts of Ca, Al and Fe, it did not record the largest retention capacity. The largest retention capacity was recorded by HV2. This could be due to the fact that, AC recorded the largest amount of total phosphorus since it is a phosphate fertilized farm. This could lead to some of its adsorption sites already being occupied with P particles. That HV2 recorded a lower pH value of 5.8 and greater organic matter content could also explain its largest retention capacity.

The influence of Al and Fe is greater at a lower pH level and a larger amount of organic carbon (Darke and Walbridge, 2000). At a low pH, more Fe^{2+} and Al^{3+} are able to move into solution, and hence precipitation of P by Fe^{2+} and $\text{Fe}(\text{OH})_3$ is also increased to aid in the formation of $\text{Fe}(\text{OH})_2\text{H}_2\text{PO}_4$ which is an insoluble P salt. Positive effects of organic matter have also often been attributed to the inhibition of oxide crystallization by organic molecules which contribute to an increase in the proportion of Fe and Al. (Darke and Walbridge, 2000). An increase in Al and Fe will then lead to an increase in P retention. At low pH, phosphate can be adsorbed by protonated amino groups. Organic matter also stimulates P sorption by stabilizing Al/Fe surfaces and promotion of new anion sorption sites (Kwang and Thiang, 1979).

Soil HP recorded the least amounts of clay, Fe and Al. Soil HP is of a very sandy nature and this could also have resulted in its low sorption property. Sandy soils adsorb less because they usually have a rough uneven surface.

Organic matter can be said to have shown no differences on the sorption process of the other soils used (HF, AC and HP). This is because they recorded almost the same amounts of organic matter (Table 4.1).

In this study, because the physical properties of the soil with respect to their depth was almost similar, there was not much difference in the amounts of P adsorbed at different depths of soils studied. The only deviation was recorded by soil HV whose subsurface soil HV2 (10-20 cm) adsorbed more P than HV1 and HV3 (0-10 cm). From Table 4.1, HV2 contained the largest amounts of both Al and Fe.

4.3 PHOSPHORUS ADSORPTION ISOTHERM INDICES

The P sorption data was fitted to Freundlich, Langmuir and Temkin equations. The main objective in doing this was to summarize the adsorption properties of the soils by using a few parameters to understand the adsorption process and to obtain a value for adsorption maximum for all the soils.

There were good fit of the data to the Temkin, Freundlich and Langmuir equations. Linear correlation coefficient (r^2) values ranged from 0.976 – 0.990 for Langmuir equation, 0.920 to 0.990 for Freundlich and 0.802 to 0.980 for the Temkin equations.

4.3.1 LANGMUIR ISOTHERM

This was first used to study P adsorption in soils by Olsen and Watanabe in 1957. Langmuir sorption isotherm equation provides both an estimate of sorption capacity and an estimate of the average sorption strength of the soil (Olsen and Watanabe, 1957; Pant and Reddy, 2001). It also provides a quantitative estimate of the effect of soil conditions on P sorption (Vadas *et al*, 1999). The Langmuir equation in its linear form can be written as

$$\frac{C}{X} = \frac{1}{bK_{max}} + \frac{C}{K_{max}}$$

Where C = equilibrium concentration of P in solution ($\mu\text{g P/mL}$),

X= mass of P adsorbed (μg) /mass of soil (g)

K_{max} = adsorption maximum ($\mu\text{g P/g soil}$),

b = an empirical parameter related to bonding energy of soil for phosphate.

A plot of C/X against C should give a straight line, from which the adsorption maximum K_{max} which is the inverse of the slope and the constant b (slope/intercept) related to energy of adsorption or bonding energy can be easily calculated.

The useful parameters normally obtained from Langmuir plots are:

Adsorption maximum (K_{max})

Bonding energy (b)

Maximum buffering capacity (bK_{max}).

In this study, Langmuir plots for the soils were obtained by plotting the values C/X against the equilibrium P concentrations. The various plots are presented in Figures 4.6, 4.7, 4.8 and 4.9. The useful parameters were calculated and are presented in Table 4. 3. together with their respective correlation coefficients.

Though the soils conformed well to the Langmuir equation, some showed a slight curve at the upper end of the plot. The three soils of HP1, HP2, HP3 and HF1 (0-10 cm of HF) exhibited this behavior. This curve was attributed to strong adsorbing sites.

Using r^2 values as a test for goodness of fit, r^2 was greater than 0.9 for all the soils implying that the soils' data did conform to the Langmuir equation and that

adsorption did occur by a single process. Deviations from Langmuir plot may be attributed to the migration of the adsorbed P to sub-surface layers. (Bache and Williams, 1971). For this study, the Langmuir equation was able to satisfactorily describe P adsorption at all levels of added P (51 -574 $\mu\text{g/g}$). Harter and Baker (1977) considered the effect of adsorbed ions in the equilibrium solution as the cause of the commonly reported curvilinear nature of the simple Langmuir isotherm.

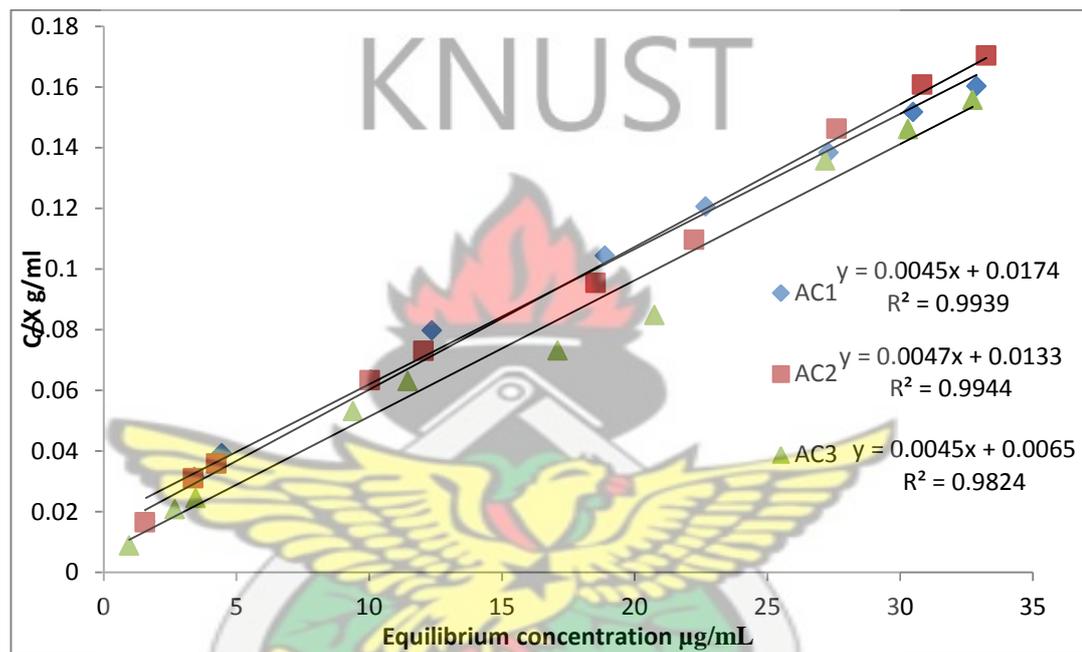


Fig 4.6: Langmuir Isotherm for soil AC

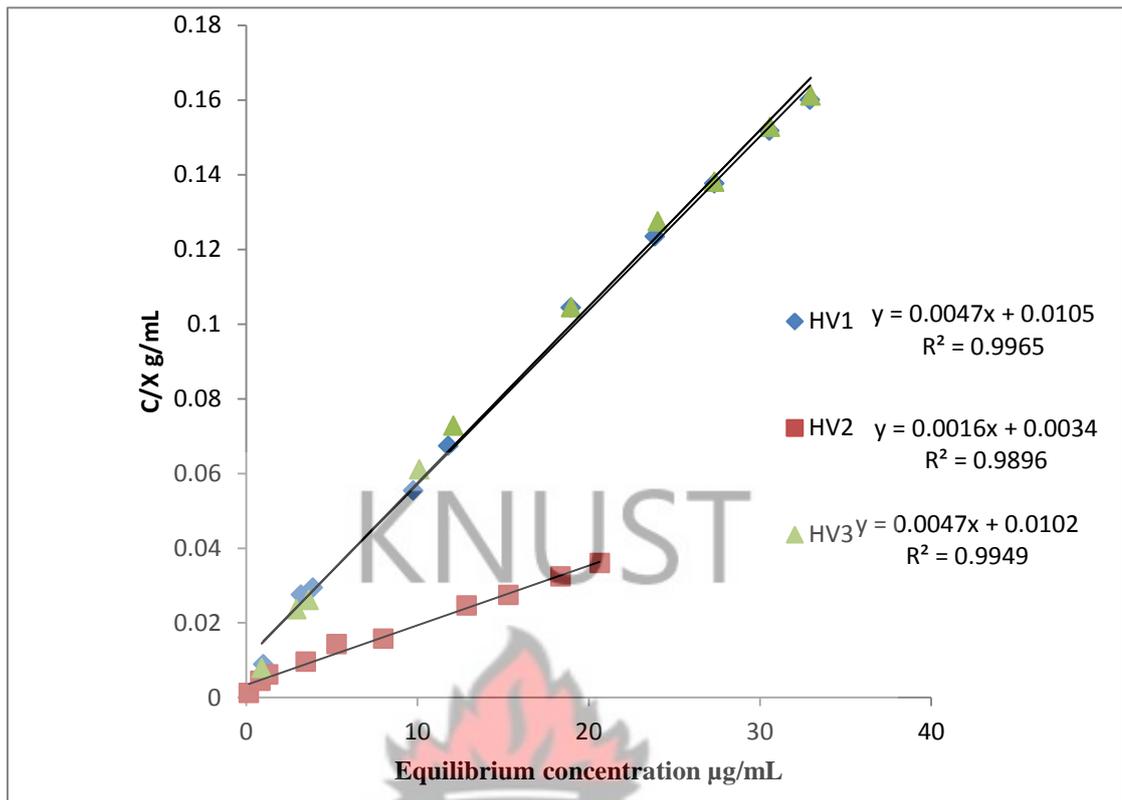


Fig 4.7: Langmuir Isotherm for soil HV

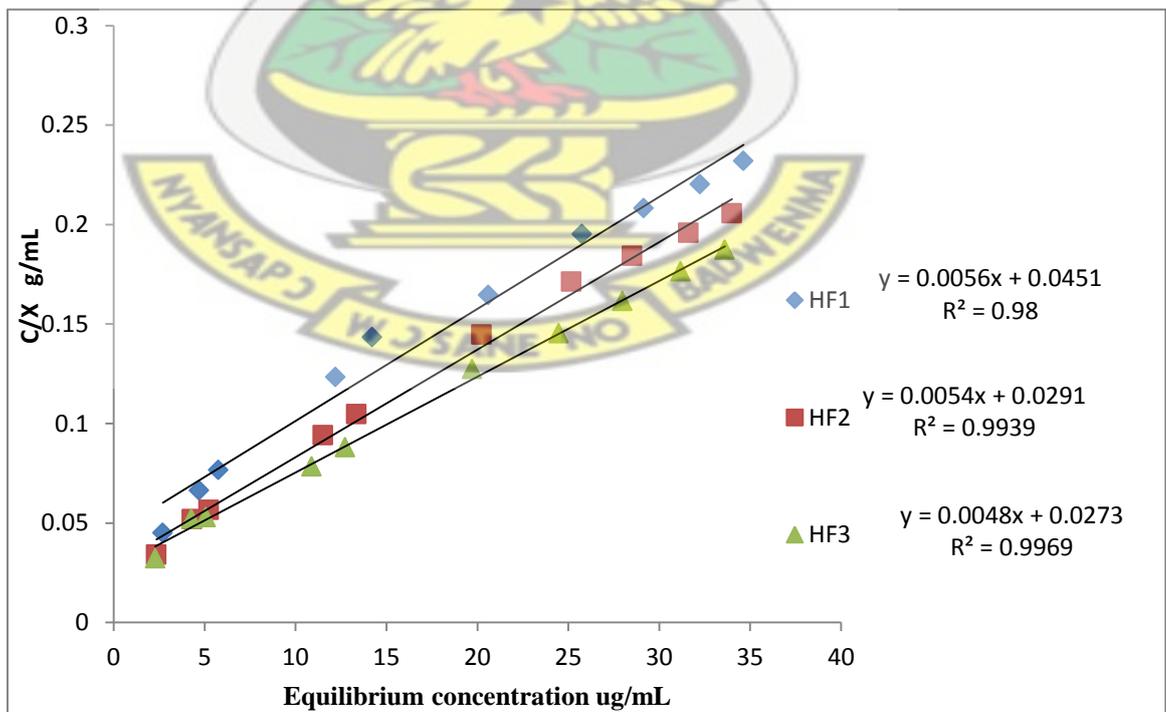


Fig 4.8: Langmuir Isotherm for soil HF

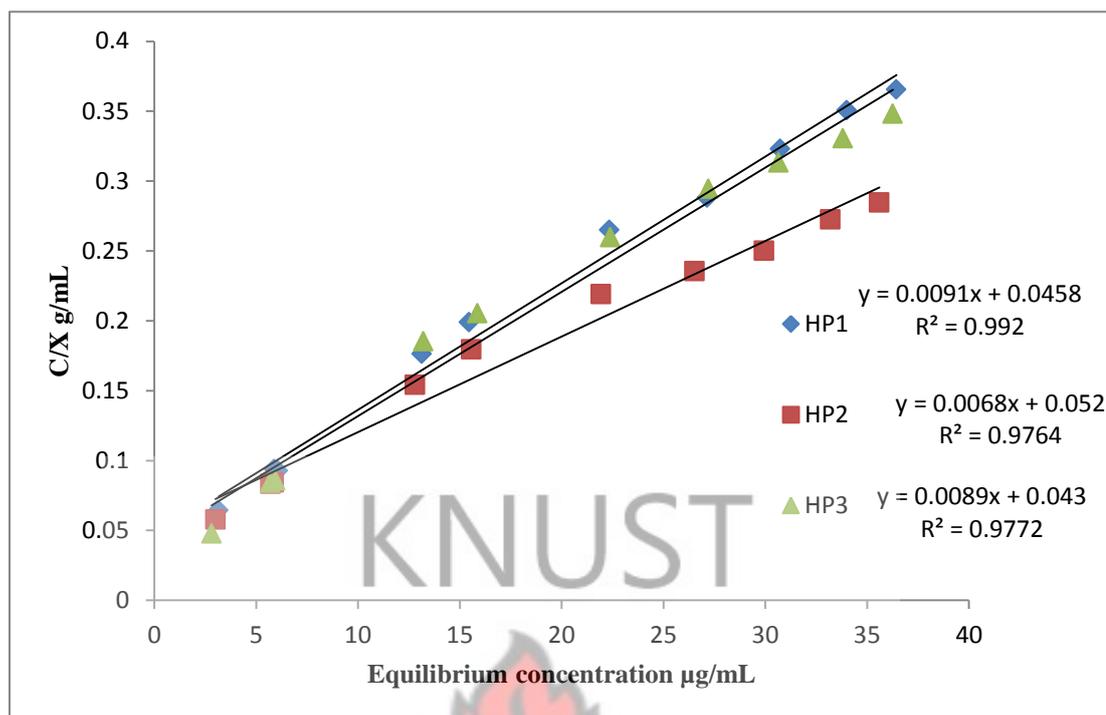


Fig 4.9: Langmuir Isotherm for soil HP

Table 4.3: Phosphorus sorption parameters from the Langmuir model

Soil	Depth (cm)	Bonding Capacity (b) mL μ g $^{-1}$	Adsorption Max (K_{max}) μ g g^{-1}	Max. Buffering Capacity (bK_{max})	r^2
AC	1 0-10	0.259	222.222	57.467	0.994
	2 10-20	0.353	212.768	75.187	0.994
	3 30-40	0.692	222.222	153.847	0.982
HV	1 0-10	0.162	212.766	34.447	0.997
	2 10-20	0.471	625.000	294.125	0.990
	3 20-30	0.461	212.767	98.040	0.995
HF	1 0-10	0.125	178.571	22.179	0.980
	2 10-20	0.186	185.185	34.370	0.994
	3 20-30	0.176	208.333	36.625	0.997
HP	1 0-10	0.199	109.890	21.835	0.992
	2 10-20	0.131	147.059	19.235	0.976
	3 20-30	0.207	112.360	23.247	0.977

They further stated that when a second species is desorbed, reaction of the adsorbate with the surface will be altered, depending upon the concentration of the desorbed species in solution. Poor fit of the Langmuir isotherm to adsorption data has been attributed to the presence of different types of sites on the adsorbent surface (Syers *et al.*, 1973; Posner and Bowden, 1980).

4.3.1.1 Adsorption Maximum (K_{max})

K_{max} is used to estimate the amount of phosphate fertilizer needed to be added to an unfertilized soil. It is reported to be the most important parameter for characterizing the P adsorption of soils (Rajan, 1973). It is mainly because of this parameter that the Langmuir equation is the preferred equation. It is calculated as the inverse of the slope of the Langmuir plot ($K_{max}=1/slope$).

In this study, K_{max} varied amongst all the soils. It ranged from 112.36 $\mu\text{g/g}$ to 635 $\mu\text{g/g}$. The maximum adsorption values of the soils were similar with respect to depth. For example, AC1 (0-10cm) and AC3 both recorded a value of 222.2 $\mu\text{g/g}$ whilst AC2 recorded 212.768 $\mu\text{g/g}$. The only deviation that occurred was for soil HV. The sub surface HV2 recorded a value of 635 $\mu\text{g/g}$, which was about 194% greater than that recorded by both the topsoil and the surface soil.

Soil HP recorded the least K_{max} values, probably because of the comparatively lower levels of aluminium and iron. It is possible that the fertilization history of this particular plantain farm affected its P sorption characteristics. No form of phosphate was ever applied. Soil HP also had a coarse soil texture (had a greatest percentage of sand and silt) which reduces the number of adsorption sites. HP1 recorded a K_{max} value which was about 469% less than that recorded by HV2.

The very low K_{\max} recorded by HP soils implies that their adsorption sites cannot retain high quantities of P, and as such may be more available to plants if P was applied. Adversely the excess of the P applied or the un-adsorbed P could be lost as run-off to water bodies which could cause eutrophication and algal bloom in the water bodies. Generally to enhance plant growth, less fertilizer will be needed for soil HP than HV.

K_{\max} values obtained from this study are smaller than those reported by Anghinoni *et al.*, (1996) for Appalachian acidic soils and quite comparable to those obtained by Ahmed *et al.*, (2008) for some Australian soils. They were also much higher than those obtained by Onweremadu and Ofoh, (2007) for some Nigerian soils and those that were obtained by Opoku-Agyemang (2006) for some soils from the Ashanti Region of Ghana. Fontes (1988) reported an average value of $4482 \mu\text{g P g}^{-1}$ for K_{\max} of Brazilian soils derived from sandstone, clay stone, mafic rock and schist. On the other hand Siradz (2009) found the K_{\max} value for red soils from Lampung, West and Central Java, Indonesia as $2000 \mu\text{g P g}^{-1}$. Clearly there is a large variation of K_{\max} values both within and between soil types probably because of the differences in the physical and chemical characteristics of the soils.

For soils that retained so much, adsorption can be reduced by up to 40% by adding strongly chelating ligands like malate and citrate to the soils (Anthonio *et al.*, 2002). These ligands (citric and malate) can form complexes with Fe^{3+} and Al^{3+} , leaving the phosphate in the soil free, mobile and available for plant uptake. This could be applicable to soils AC and HV in this study.

4.3.1.2 The Bonding energy (b)

The bonding energy or capacity (b) shows comparatively how strongly the added phosphorus is adsorbed on or released from the adsorbing surface. The bonding

energy is derived from the slope and the intercept of the Langmuir isotherm equation ($b = \text{slope/intercept}$).

Bonding energies of the soils studied ranged from 0.125 Lmg^{-1} to 0.692 Lmg^{-1} . The largest bonding energy was recorded by the sub- soil AC3 and the least was also recorded by HF1 (Table 4.3).

Bonding energies ranging from $0.91 - 4.31 \text{ Lmg}^{-1}$ have been reported by Oskay (1986). Onweremadu and Ofoh (2007) reported an average value of 0.8 Lmg^{-1} for some Nigerian soils which is higher than the mean of 0.285 Lmg^{-1} obtained from this study

4.3.1.3 Maximum Buffering Capacity (bK_{max}).

Maximum buffering capacity for soils is the product of the adsorption maximum and binding energy ($b \times K_{\text{max}}$). Maximum buffering capacity is a capacity factor and measures the ability of the soil to replenish phosphate ions to soil solution as they are depleted. In this study, Soil HV2 had the largest bK_{max} value of 294.125, the least value was recorded by all the soils from HP.

4.3.2 FREUNDLICH ISOTHERM

The Freundlich equation was the first model to be used in describing phosphate retention (Russell and Prescott, 1916). Before the Langmuir equation was used to describe P adsorption in 1957 by Olsen and Watanabe, the Freundlich equation was commonly used for describing phosphate adsorption data (Barrow, 1978). The Freundlich equation is normally used in its logarithmic form i.e

$$\log X = 1/n \log C + \log a$$

C = equilibrium P concentration

$X = \text{mass of P adsorbed } (\mu\text{g}) / \text{mass of soil (g)}$

The Freundlich isotherm was applied to adsorption data by plotting $\log X$ against $\log C$. From the equation, the parameters of importance are:

Sorption capacity (a)

P sorption energy (n)

The sorption capacity, (a) which is a measure of sorption surface is indicative of the number of sorption sites. It is obtained from the intercept of the curve. The sorption energy (n) which relates to the energy of sorption was obtained from the slope of the curve. The Freundlich equation implies that the energy of adsorption decreases exponentially with increasing saturation of the surface. It has been proposed that sorption capacity could be considered as a capacity factor, implying that a soil having a large sorption capacity value has a great adsorbing capacity.

The various plots are presented in Figures 4.10, 4.11, 4.12 and 4.13. The useful parameters were calculated and are presented in Table 4. 4. together with their respective correlation coefficients.

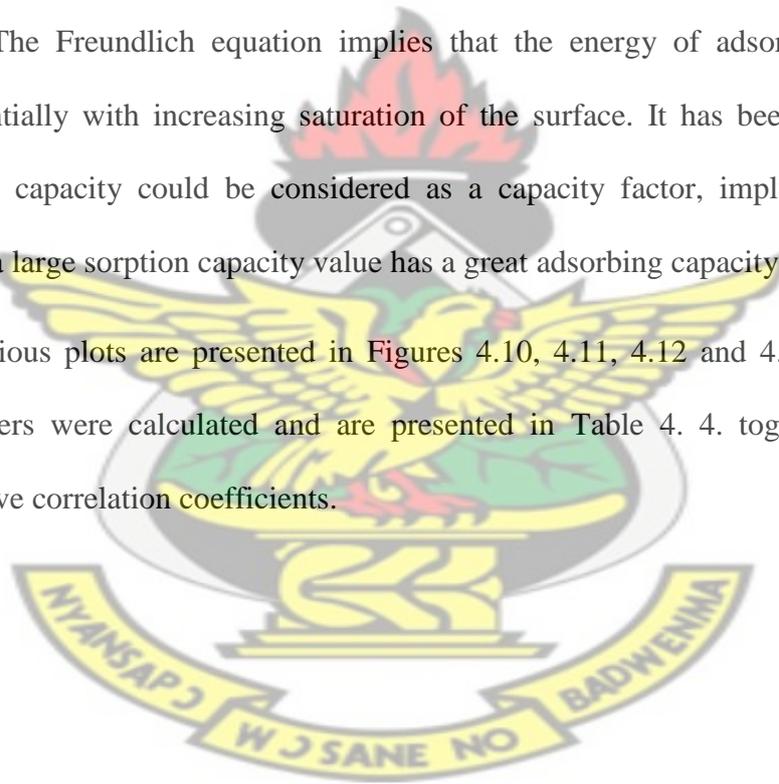


Table 4.4: Values of Phosphorus Sorption Parameters from the Freundlich model.

Sample	Depth (cm)	Sorption capacity (a) $\mu\text{g g}^{-1}$	Sorption energy (n)	r^2	
AC	1	0-10	80.705	3.691	0.987
	2	10-20	85.428	3.942	0.960
	3	20-30	114.604	5.048	0.868
HV	1	0-10	105.609	5.244	0.940
	2	10-20	224.388	3.068	0.968
	3	20-30	111.918	5.988	0.940
HF	1	0-10	40.983	2.721	0.990
	2	10-20	54.026	3.075	0.996
	3	20-30	54.866	2.815	0.974
HP	1	0-10	38.415	3.764	0.974
	2	10-20	37.601	3.011	0.980
	3	20-30	47.044	4.796	0.922

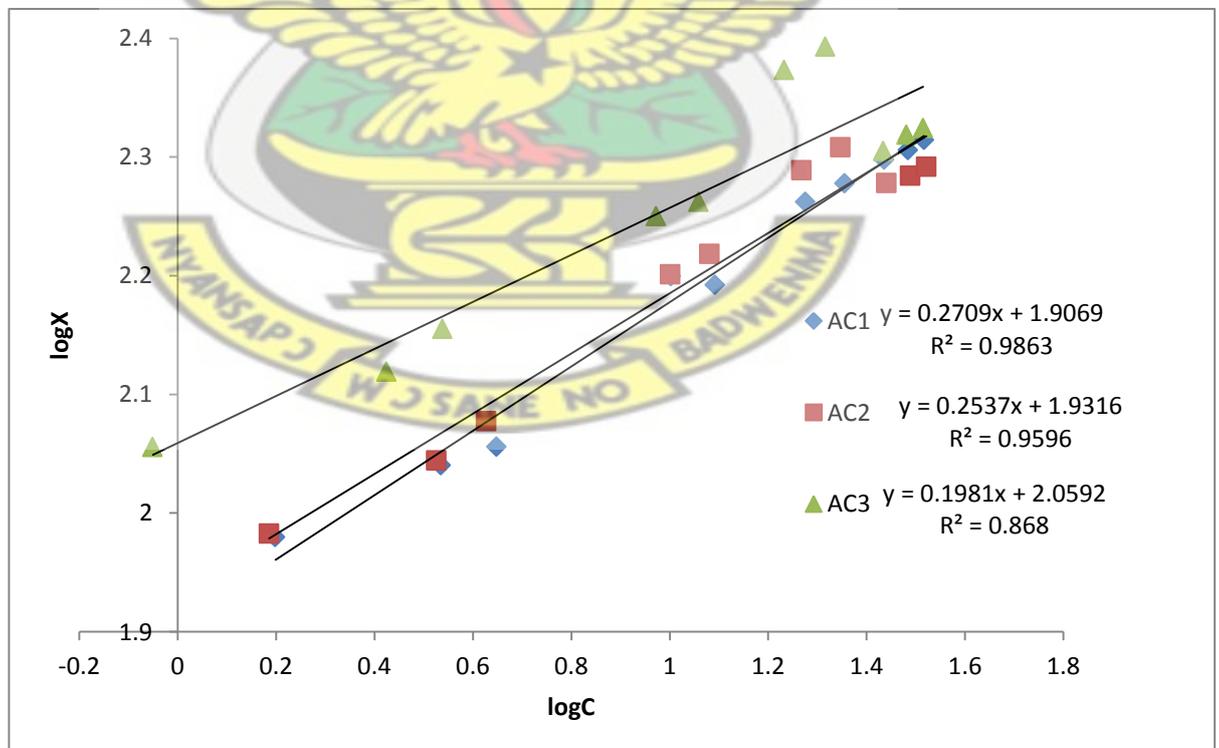


Fig 4.10: Freundlich isotherm for soil AC

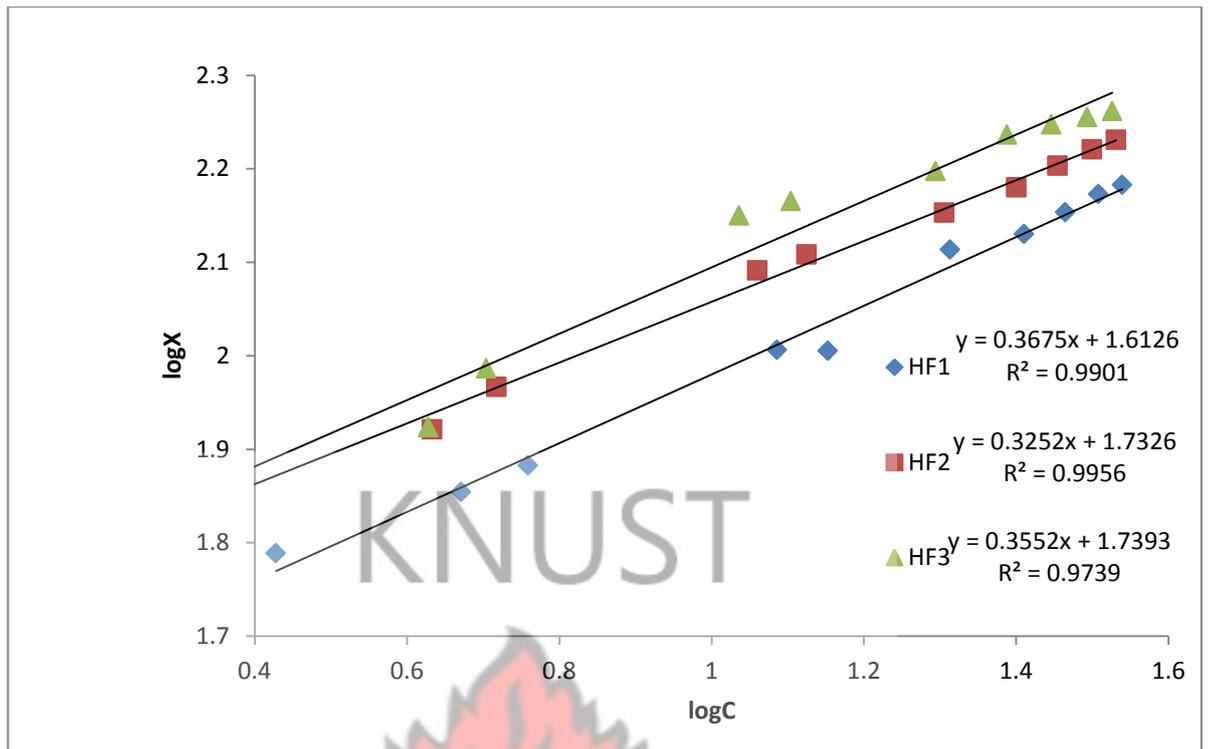


Fig 4.11: Freundlich isotherm for soil HF.

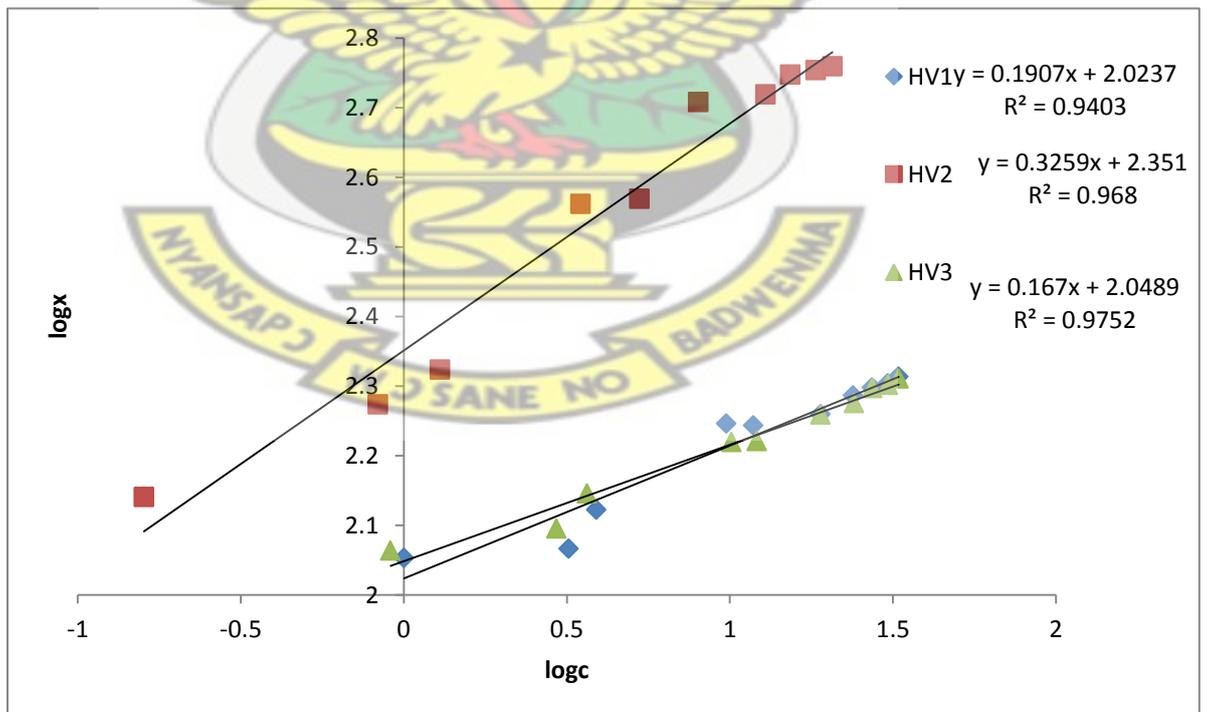


Fig 4.12: Freundlich isotherm for soil HV.

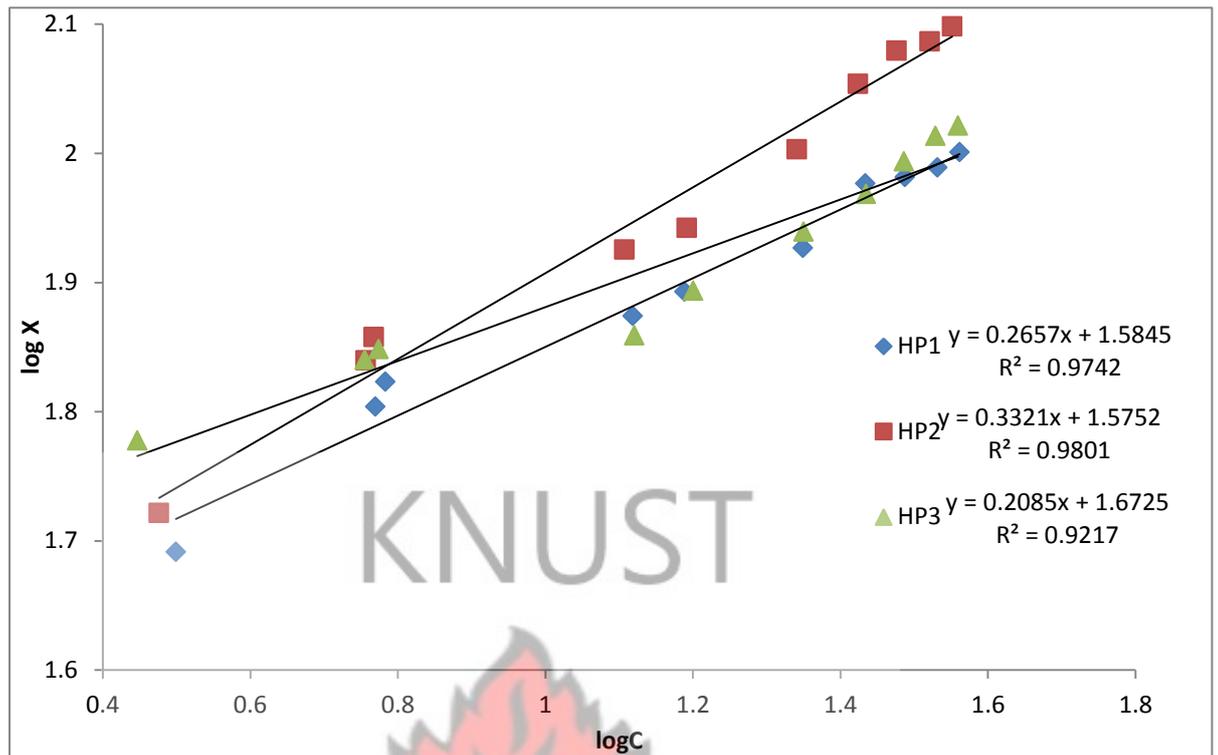


Fig. 4.13: Freundlich isotherm for soil HP

In some of the soils studied, the lines were gently curved at higher P concentrations which indicate no further adsorption at that point. This was exhibited by HP1 (Fig. 4.12.). Freundlich equation for all the soil samples studied showed another characteristic. The adsorption points were compressed at the top end, which might have disguised the poor linearity. Bache and Williams (1971) and Barrow (1978) reported gentle curves when Freundlich equation was applied to their soil phosphate adsorption data.

From Table 4.4, the largest sorption capacity of $224.4\mu\text{gg}^{-1}$ value was obtained by HV2 and the least value of $37.6\mu\text{gg}^{-1}$ was recorded by HP2. This implies that HV2 has the largest amount of adsorption sites which agrees with its adsorption maximum value obtained from the Langmuir equation.

4.3.3 TEMKIN ISOTHERM.

The Temkin equation has also been used by several authors to describe P sorption (Ahmed *et al.*, 2008, Anghinoni *et al.*, 1996, Ioannou *et al.*, 1998). The Temkin equation is written as:

$$X/m = a + B \ln C$$

Where X = mass of P adsorbed (μg)/mass of soil (g)

C is the equilibrium P concentration in $\mu\text{g/mL}$, 'a' is a constant and B is considered as a buffering capacity of the soil.

The Temkin plot was obtained by plotting the mass of P adsorbed per gram of soil ($\mu\text{g g}^{-1}$) against the natural logarithm (\ln) of the equilibrium concentration (mg/L).

Temkin plots of the various soils are presented in Figures 4.14, 4.15, 4.16 and 4.17

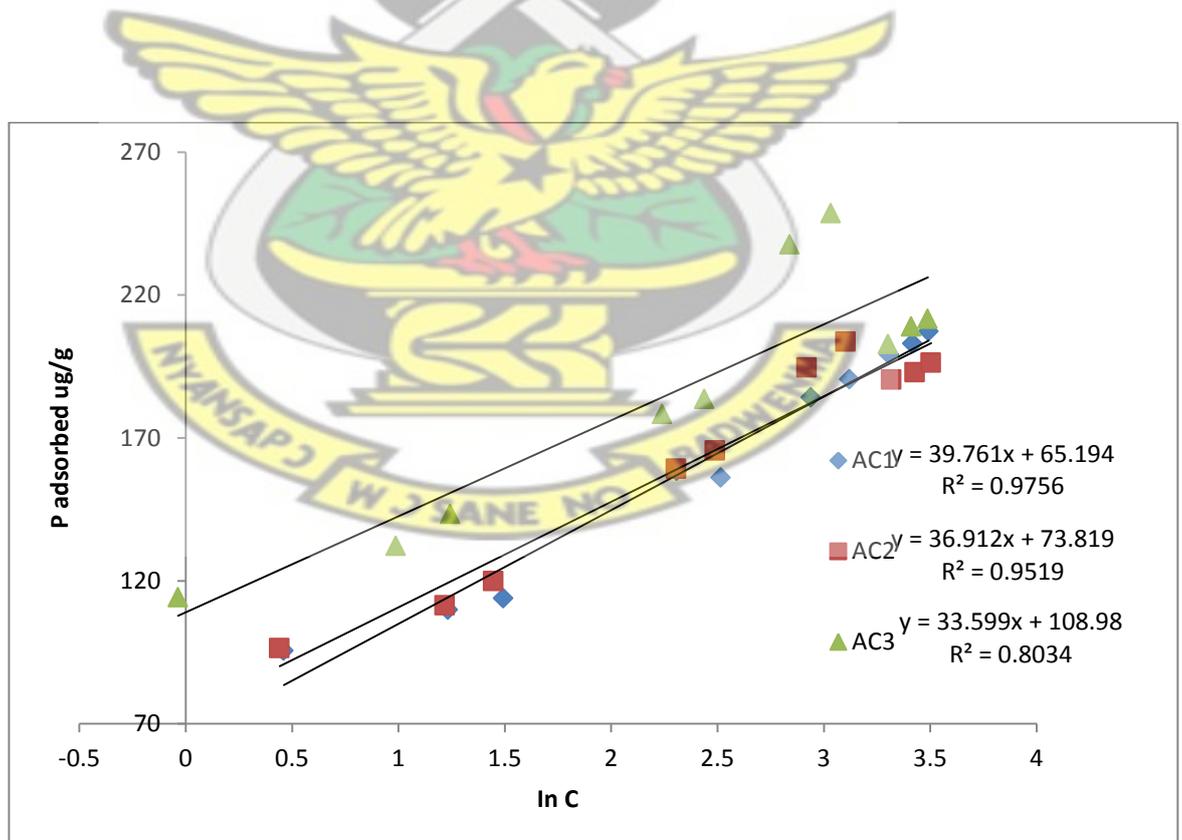


Fig 4.14: Temkin isotherm for soil AC.

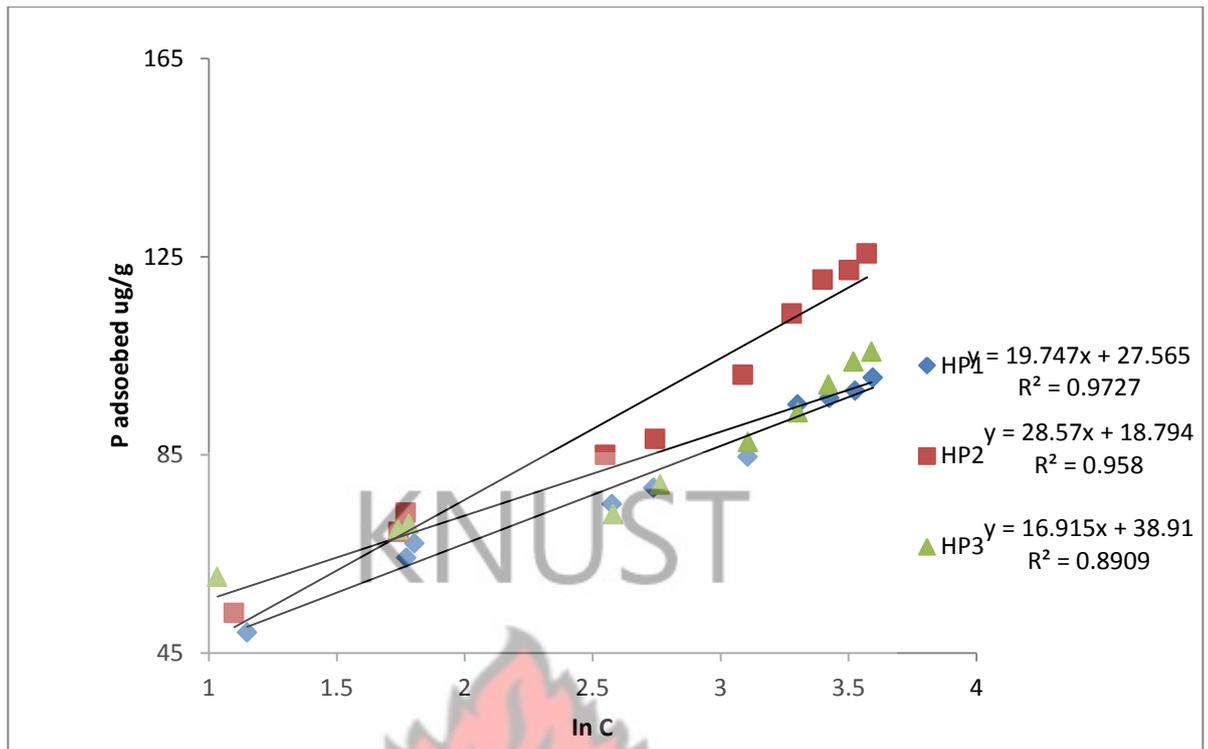


Fig 4.15: Temkin isotherm for soil HP

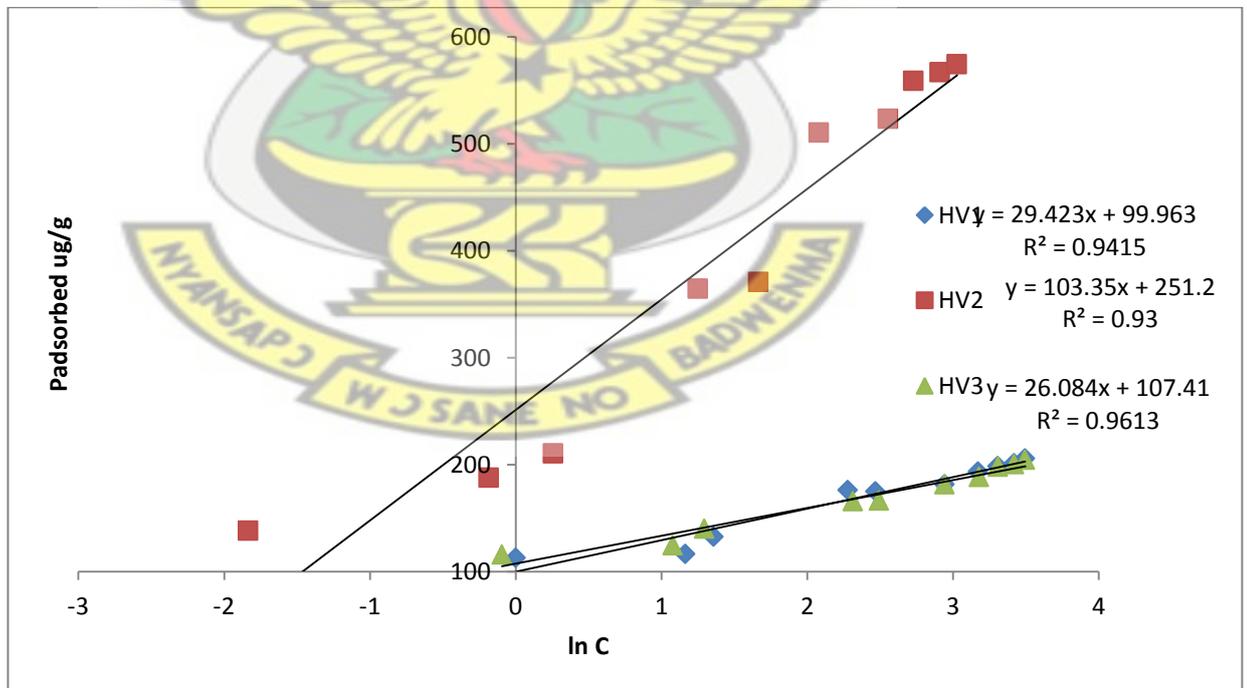


Fig 4.16: Temkin isotherm for soil HV

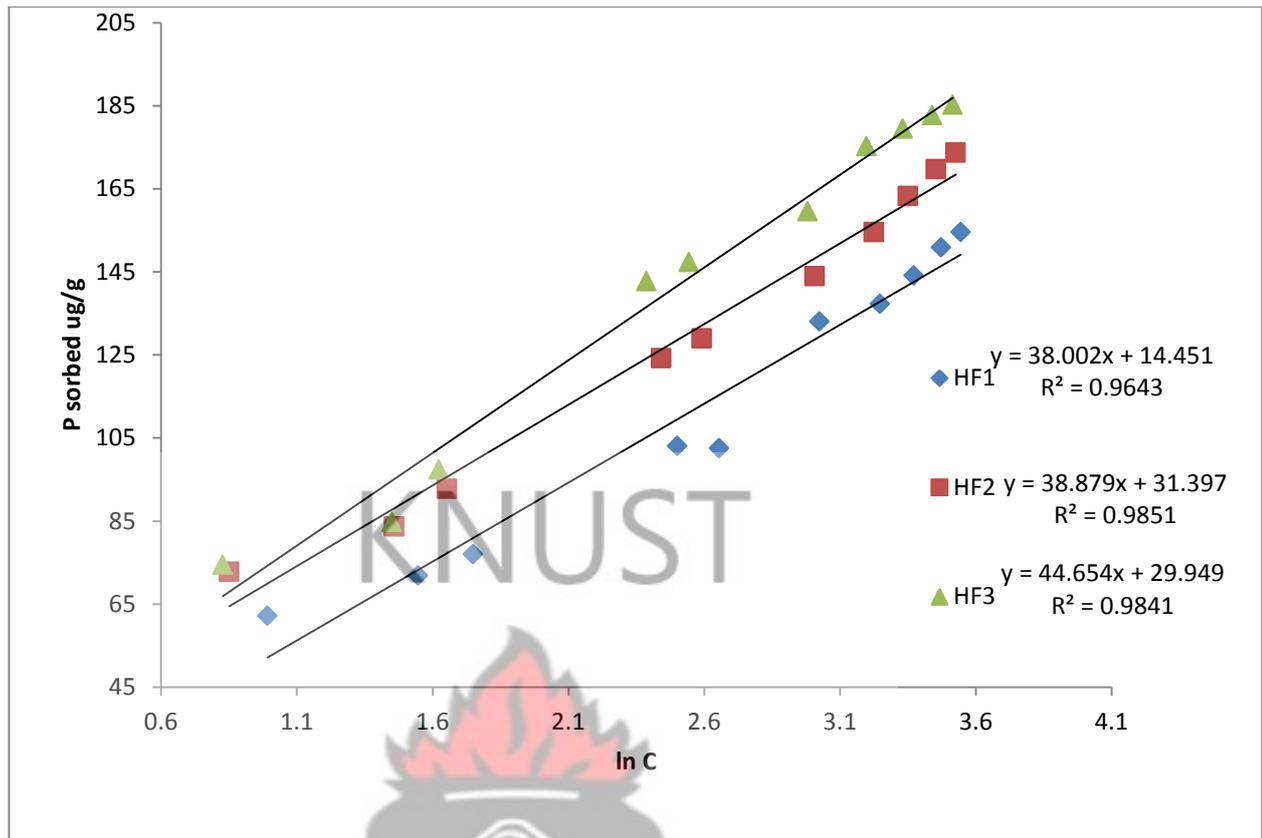


Fig 4.17: Temkin isotherm for soil HF.

The slope of the curve is considered as the buffering capacity (B) of the soil. Differences in buffering capacities were noted among the soils studied.

Table 4.5 shows that the largest buffering capacity was recorded by the sub- surface soil HV2. It recorded a value of 103.35 which was 250% more than that of its top soil and 296% more than that of its sub- soil. This difference can be attributed to the pH and variations in the amounts of iron and aluminium of the various soils. The least buffering capacity was recorded by soil HP. The value recorded by HP3 was 511% lower than that of HV2.

Table 4.5: Buffering Capacities

Sample	Depth(cm)	Buffering capacity (B)	
AC	1	0-10	39.761
	2	10-20	36.912
	3	20-30	33.599
HV	1	0-10	29.423
	2	10-20	103.35
	3	20-30	26.084
HF	1	0-10	38.002
	2	10-20	38.879
	3	20-30	44.654
HP	1	0-10	19.747
	2	10-20	28.57
	3	20-30	16.915

The higher or stronger the buffering capacity, the larger the proportion of P in solid phase relative to solution phase; increasing buffering capacity also lowers the rate of dissolution or desorption of P from the solid phase and vice versa (Holford, 1989).

The buffering capacities of soil AC at different depths were very close, AC1 recorded a value of 39.761, AC2 recorded a value of 36.912 and AC3 recorded 33.599.

In acidic soils, the amounts of aluminium and iron affect the buffering capacity the most. From the pH values obtained for the soils studied, the soils can be said to range from acidic to slightly neutral (the pH ranged from 5.58 to 7.77). The buffering capacities of the soils obtained from the Temkin plot were in the same order as their adsorption maxima (K_{max}) obtained from the Langmuir plot which confirms a report

by Rajan (1973) that soils with high adsorption maxima (K_{max}) have high buffering capacities.

Buffering capacity is recognized as the phosphate-retention characteristic of the soil. It is the indication of the ability of the soil to replace a unit change in soil solution P and maintain a productive solution concentration. The significance of buffering capacity in characterizing phosphate availability to plants has been demonstrated by many investigators (Olsen and Watanabe 1963; Mattingly 1965; Barrow 1967; Holford and Mattingly 1976).

Buffering capacity has also been related to the phosphate fertilizer requirements of soils (Ozanne and Shaw 1968). In the process of diffusion, P is desorbed from the soil of high concentration and transported to the unfertilized soil (Bhadoria *et al.*, 1991). In conducting an experiment to determine soil phosphate diffusion coefficients, Bhadoria *et al.*, (1991) found that P diffusion coefficient is dependent on the buffer power, desorption or adsorption of P and the time available for reaction. Therefore since the buffering capacity was least in the HP soil, it is expected that the diffusion of P would be faster in this soil compared to the other soils. As the HV soil has the largest buffering capacity, P diffusion would be slowest in this soil. For this reason, more P fertilizer may be needed in the HV soil to obtain a good yield.

4.4 CORRELATION ANALYSIS

It is expected that some P adsorption parameters would be correlated with soil properties (Olsen and Watanabe, 1957; Stuanes, 1982). Phosphorus sorption behaviour is not necessarily controlled by all, or any of the properties because some of the properties are inter correlated and may have reflected in the correlation

analysis. The analysis, although not necessarily implying cause-effect relationships, suggests the possible influence of soil components on P sorption. Knowledge of the possible effects or influence of soil characteristics on P sorption makes it easier to understand why various soils adsorb different amounts of phosphorus at different equilibrium concentrations. To make the relationships easier to interpret, correlations were considered depth-wise and correlation coefficients represented in Tables 4.6.1.1 to 4.6.1.3

4.4.1 CORRELATION BETWEEN SOIL PROPERTIES AND SOME PARAMETERS OF THE PLOTS

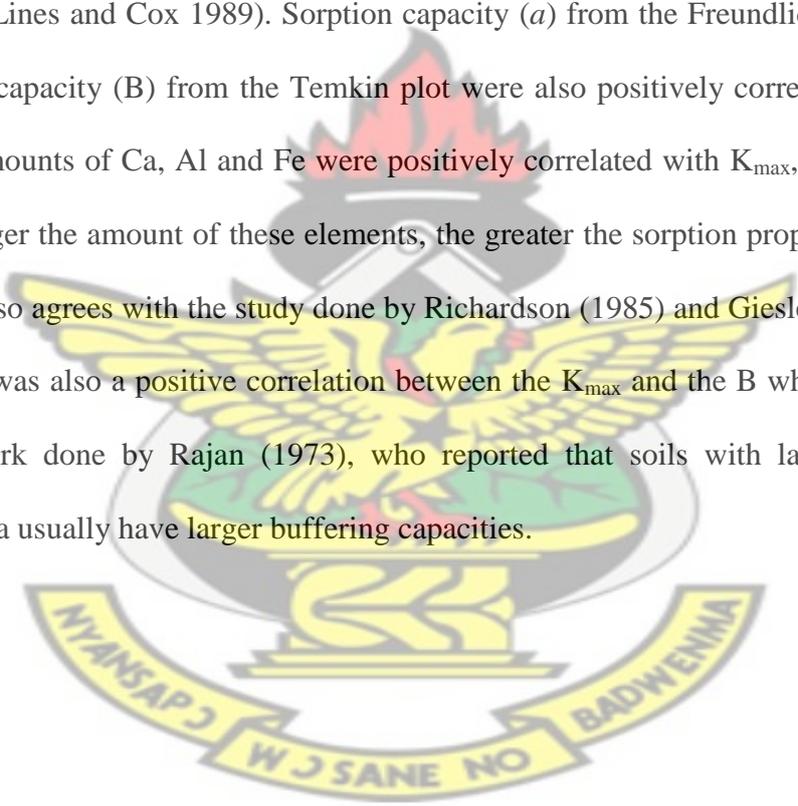
4.6.1.1 Correlation coefficients for top soils used (0-10cm)

	pH	OM	clay	Fe	Ca	Al	b	K _{max}	bK	a	n	B
pH												
OM	.095											
clay	.278	.168										
Fe	.182	-.018	.920**									
Ca	.562	.011	.702*	.630*								
Al	.022	.010	.905**	.958**	.629*							
b	.122	-.374	.386	.415	.158	.442						
K _{max}	.007	.475	.791**	.639*	.639*	.723**	-.70					
bK	.147	.054	.899**	.833**	.595*	.892**	.683*	.654*				
a	-.013	.331	.690*	.638*	.495	.756**	.336	.726**	.757**			
n	-.049	-.114	-.02	.054	-.08	.142	.630*	-.188	.273	.502		
B	.023	.438	.686*	.515	.582*	.561	.248	.930**	.479	.424	.520	

**-correlation is significant at 0.01 level (2-tailed)

*-correlation is significant at 0.05 level (2-tailed)

There was no significant correlation between the pH, organic matter and any of the parameters obtained from the plots; this probably implies that these soil properties played no role in the sorption process. There was however a significant positive correlation between the amount of clay present and the amounts of Fe, Ca and Al. Clay was also significantly correlated to the K_{max} and bK_{max} from the Langmuir plot and Freundlich sorption capacity (a), which suggests that the clay content affected P sorption in the topsoil. Positive correlation between clay and K_{max} has been identified by other workers (Ryan *et al.*, 1985; Boreo *et al.*, 1988; Pena and Torrent 1990; Lines and Cox 1989). Sorption capacity (a) from the Freundlich equation and buffer capacity (B) from the Temkin plot were also positively correlated with clay. The amounts of Ca, Al and Fe were positively correlated with K_{max} , suggesting that the larger the amount of these elements, the greater the sorption property of the soil. This also agrees with the study done by Richardson (1985) and Giesler *et al.*, (2005). There was also a positive correlation between the K_{max} and the B which agrees with the work done by Rajan (1973), who reported that soils with larger adsorption maxima usually have larger buffering capacities.



4.4.1.2 Correlation coefficients for sub surface soil (10-20cm).

	pH	OM	clay	Fe	Ca	Al	b	K _{max}	bK _{max}	a	n	B
pH												
OM	.053											
clay	-.080	-.054										
Fe	.295	.065	.772**									
Ca	.743**	.355	.162	.580*								
Al	.140	.193	.775**	.949**	.533							
b	.061	.404	.438	.563	.647*	.709**						
K _{max}	-.307	.662*	.063	.208	.208	.339	.568					
bK _{max}	-.204	.647*	.120	.310	.359	.466	.757**	.956**				
a	-.239	.682*	.233	.371	.332	.541	.755**	.954**	.984**			
n	.089	.126	.645*	.580*	.330	.719**	.553	-.088	.088	.196		
B	-.244	.686*	.052	.180	.222	.326	.618*	.939**	.956**	.931**	-.070	

** - correlation is significant at 0.01 level (2-tailed)

* - correlation is significant at 0.05 level (2-tailed)

There was a positive correlation (0.662**) between the organic matter present in the subsurface soils and the K_{max} of the soil, which suggests that the subsurface soil organic matter favoured P sorption. This probably means that for the sub surface soil there was the inhibition of oxide crystallization by organic molecules which contributed to an increase in the proportion of Fe and Al which further led to an increase in sorption. (Borggaard *et al.*, 1990; Darke and Walbridge, 2000). Organic matter was also positively correlated with the maximum buffering capacity, the buffering capacity and the sorption capacity obtained from the Freundlich plot.

There was no significant correlation between clay and K_{max} for the sub surface soil. The amount of clay, Fe and Al present, showed a positive correlation with the Freundlich sorption capacity. Similarly, there was a positive correlation (0.939**) between the K_{max} and the buffering capacity.

4.4.1.3 Correlation coefficients for sub soil (20-30cm).

	pH	OM	clay	Fe	Ca	Al	b	K_{max}	bK_{max}	a	n	B
pH												
OM	0.439											
clay	0.095	-0.101										
Fe	0.289	0.093	.933**									
Ca	.732**	.751**	0.175	0.345								
Al	-0.093	0.051	0.355	0.197	-.013							
b	0.094	0.062	.834**	.850**	0.039	0.253						
K_{max}	0.148	0.353	.686*	.637*	0.483	0.414	0.435					
bK_{max}	0.089	0.121	.861**	.874**	0.101	0.288	.993**	0.525				
a	0.277	0.365	.787**	.861**	0.387	0.231	.848**	.687*	.872**			
n	0.174	0.120	0.223	0.382	-.042	-0.235	.611*	-0.142	0.549	.584*		
B	0.013	0.164	0.438	0.298	0.354	0.460	0.043	.858**	0.142	0.233	-.620*	

** - correlation is significant at 0.01 level (2-tailed)

* - correlation is significant at 0.05 level (2-tailed)

Both the pH and organic matter of the surface soil did not show any significant relationship with any of the parameters obtained from the three plots. The amount of clay present correlated positively with the binding energy, adsorption maximum, buffering capacity and the Freundlich sorption capacity; implying that the clay content had a positive effect on sorption for the surface soils. The amount of Fe present correlated positively with those parameters, but the Al present showed a non-

significant relationship with them. There was a strong positive relationship between the buffering capacity and the K_{\max} (0.858**).

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CHAPTER FIVE

5. CONCLUSION

In this study, P adsorption isotherms were obtained for twelve soil samples. The slopes of the adsorption isotherm for soils were gentle to steep, covering a wide range of P sorption capacities. The isotherms were similar indicating similarity in the nature of adsorption reaction, but differed in the intrinsic characteristics such as the slopes of the isotherms and adsorption capacity. Maximum P adsorbed by the soil ranged from 49.17 to 574.26 $\mu\text{g P g}^{-1}$ soil. Differences in the amounts adsorbed may be attributed to differences in soil texture, clay mineralogy, organic matter, aluminium, iron and calcium contents in the soil. Soil from Huhunya which was virgin, adsorbed the greatest P, and the least P was also adsorbed by soil from a plantain farm in Huhunya.

In the investigation it was noted that Langmuir equation provided the best fit to P adsorption data in most of the soils compared to the Freundlich and Temkin equations. The r^2 values calculated from the Langmuir plots of 12 soils ranged from 0.976 to 0.99 with an average of 0.989, followed by the Freundlich plots with an average $r^2 = 0.958$, and Temkin plot with average $r^2 = 0.942$.

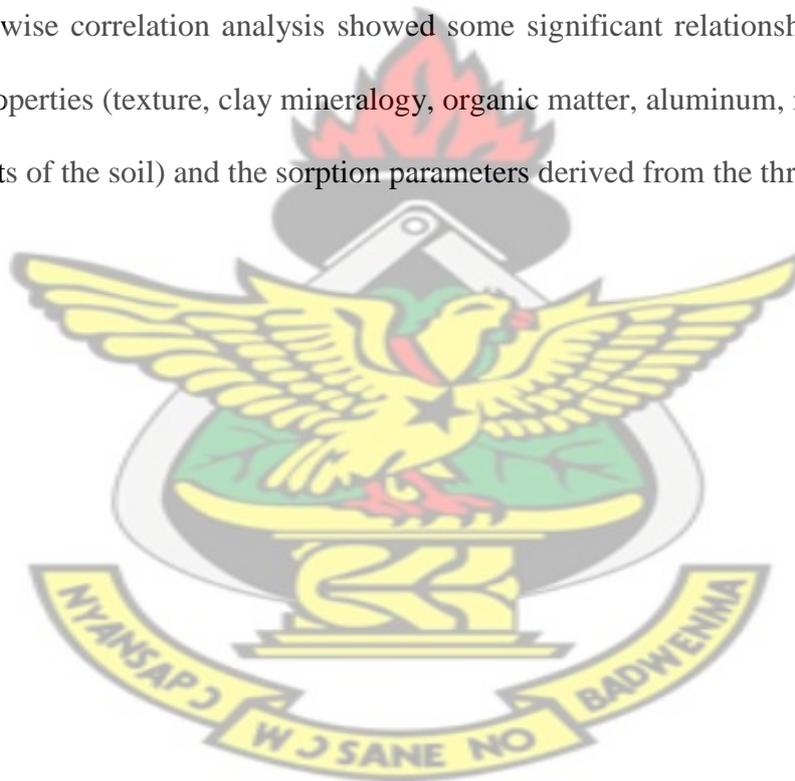
P sorption data enabled the prediction of the amount of fertilizer needed for a soil. This will prevent the arbitrary addition of fertilizer to soil which can cause eutrophication.

In an increasing order of P retention for this study, Huhunya plantain farm was less than Huhunya fallow land which was less than the Akwadum cocoa land which was also less than the Huhunya virgin land was obtained. The reverse was obtained for the amount of phosphate fertilizer that will be required by the soils used for the

study. This implies that the virgin soil from Huhunya would require the most P fertilizer due to its larger amounts of iron and aluminium. Generally to enhance plant growth, less fertilizer will be needed for Huhunya plantain farm than Huhunya virgin land. Adversely because P diffusion is faster in the the Huhunya plantain farm, the excess of the P applied or the un-adsorbed P could be lost as run-off to water bodies which could cause eutrophication and algal bloom in the water bodies.

From the physical and chemical properties of the soils studied, soils which contain larger amounts of iron, calcium and aluminium with lower pH retain more P.

Depth-wise correlation analysis showed some significant relationships between the soil properties (texture, clay mineralogy, organic matter, aluminum, iron and calcium contents of the soil) and the sorption parameters derived from the three equations.



CHAPTER SIX

6. RECOMMENDATION

There is the need for inclusion of more soil chemical, physical and mineralogical properties in predicting soil P-adsorption to enhance reliability of information.

The price of providing subsidised fertilizer in Ghana for the year 2102 alone was GHc 468 per metric tone. This study should also be extended to cash crop (eg cocoa) growing areas in order to prevent fertilizer wastage but increase yield and also reduce leaching of P into water bodies. This would reduce the cost of importing fertilizer and protect our water bodies.



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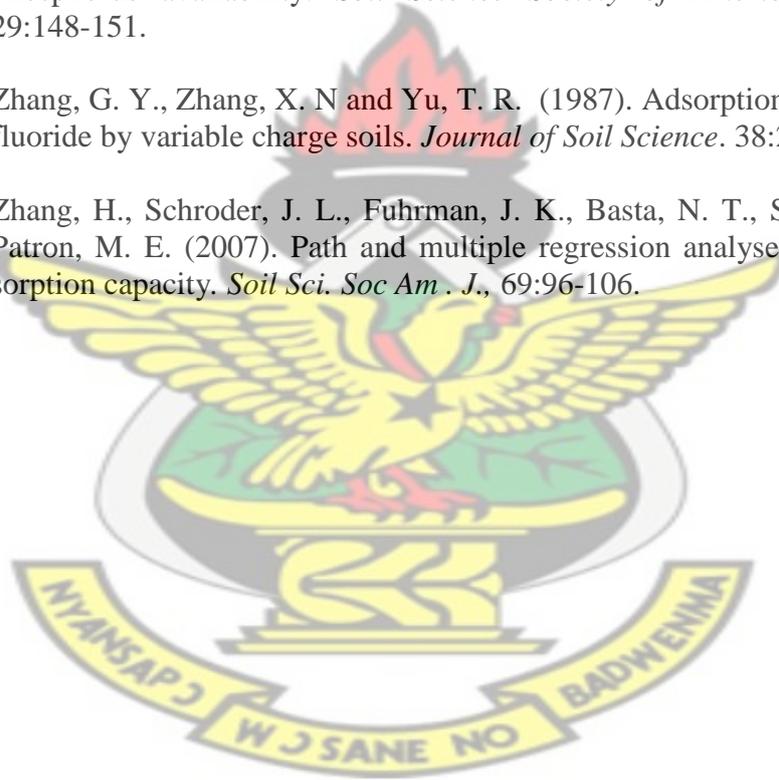
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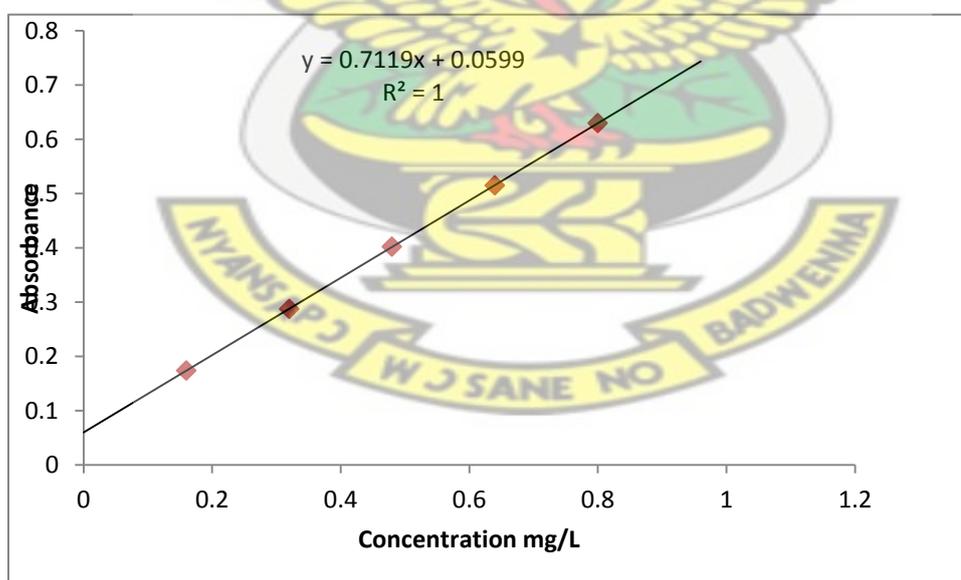
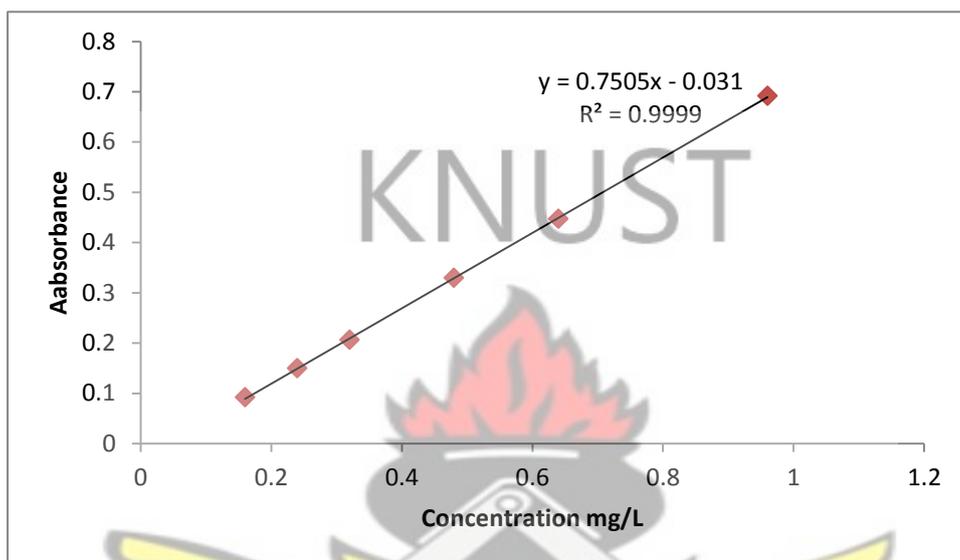
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APPENDICES

APPENDIX A

CALIBRATION CURVES USED



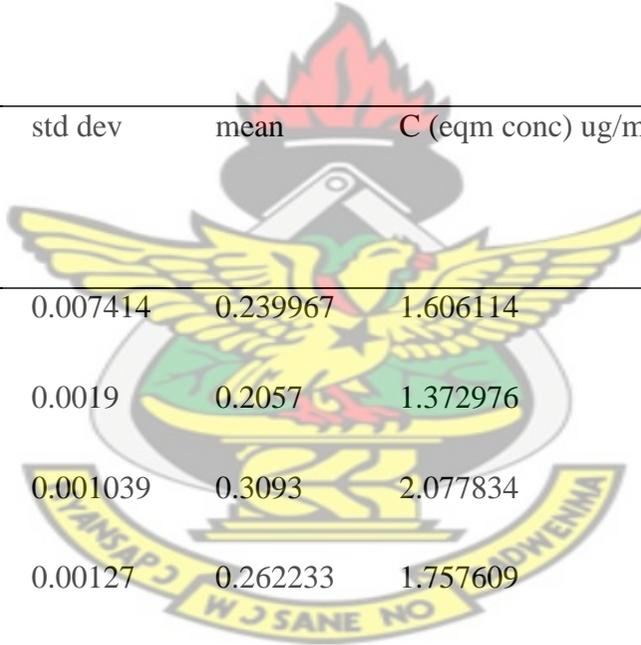
APPENDIX B

TABLES OF SAMPLES AND AMOUNTS OF P ADSORBED AT DIFFERENT EQUILIBRIUM CONCENTRATIONS

Table B.1, Concentration prepared = 5 mg/L

Actual concentration = 4.77 mg/L

KNUST



sample	A	B	C	std dev	mean	C (eqm conc) ug/mL	adsorbed conc	mass ads	C/X
								X ug/g	
A20	0.2483	0.2341	0.2375	0.007414	0.239967	1.606114	3.163886	94.91657	0.016921
A40	0.2057	0.2038	0.2076	0.0019	0.2057	1.372976	3.397024	101.9107	0.013472
A50	0.3087	0.3087	0.3105	0.001039	0.3093	2.077834	2.692166	80.76499	0.025727
A60	0.2615	0.2637	0.2615	0.00127	0.262233	1.757609	3.012391	90.37174	0.019449
A21	0.2103	0.2097	0.2097	0.000346	0.2099	1.401551	3.368449	101.0535	0.013869
A41	0.2382	0.231	0.2371	0.003879	0.235433	1.575271	3.194729	95.84187	0.016436

A51	0.196	0.1959	0.1806	0.008862	0.190833	1.271828	3.498172	104.9451	0.012119
A61	0.2851	0.3013	0.2933	0.0081	0.293233	1.968522	2.801478	84.04435	0.023422
A22	0.1287	0.1245	0.1123	0.008519	0.121833	0.802377	3.967623	119.0287	0.006741
A42	0.179	0.1836	0.179	0.002656	0.180533	1.201751	3.568249	107.0475	0.011226
A52	0.0661	0.0782	0.0747	0.006227	0.073	0.470132	4.299868	128.996	0.003645
A62	0.2095	0.2062	0.2062	0.001905	0.2073	1.383862	3.386138	101.5841	0.013623
B10	0.451	0.4533	0.4555	0.00225	0.453267	3.057332	1.712668	51.38004	0.059504
B30	0.1488	0.1535	0.1512	0.00235	0.151167	1.00195	3.76805	113.0415	0.008864
B40	0.3473	0.3386	0.3386	0.005023	0.3415	2.296911	2.473089	74.19267	0.030959
B50	0.4078	0.4053	0.4053	0.001443	0.406133	2.736654	2.033346	61.00039	0.044863
B11	0.4282	0.4279	0.4238	0.002458	0.426633	2.876128	1.893872	56.81615	0.050622
B31	0.0276	0.027	0.0275	0.000321	0.027367	0.159659	4.610341	138.3102	0.001154

B41	0.2917	0.2756	0.3095	0.016957	0.292267	1.961945	2.808055	84.24165	0.023289
B51	0.3259	0.326	0.3259	5.77E-05	0.325933	2.191001	2.578999	77.36997	0.028318
B12	0.4007	0.4015	0.4037	0.001553	0.401967	2.708305	2.061695	61.85085	0.043788
B32	0.1389	0.1359	0.1385	0.001629	0.137767	0.910782	3.859218	115.7766	0.007867
B42	0.2495	0.2741	0.2655	0.012484	0.263033	1.763052	3.006948	90.20845	0.019544
B52	0.3565	0.3546	0.3546	0.001097	0.355233	2.390348	2.379652	71.38956	0.033483
C10	0.4537	0.4452	0.4506	0.004302	0.449833	3.033973	1.843327	55.29981	0.054864
C20	0.4666	0.4651	0.4666	0.000866	0.4661	3.144646	1.732654	51.97963	0.060498
C40	0.4609	0.4643	0.4609	0.001963	0.462033	3.116977	1.760323	52.80968	0.059023
C50	0.4943	0.4943	0.4939	0.000231	0.494167	3.335601	1.541699	46.25096	0.07212
C11	0.4349	0.452	0.4439	0.008554	0.4436	2.991563	1.885737	56.5721	0.052881
C21	0.3888	0.4089	0.393	0.010602	0.3969	2.673833	2.203467	66.104	0.040449

C41	0.4681	0.4474	0.4524	0.010801	0.455967	3.075702	1.801598	54.04794	0.056907
C51	0.4883	0.4815	0.4815	0.003926	0.483767	3.264843	1.612457	48.3737	0.067492
C12	0.4248	0.404	0.4123	0.01047	0.4137	2.788134	2.089166	62.67497	0.044486
C22	0.3571	0.3571	0.358	0.00052	0.3574	2.405089	2.472211	74.16633	0.032428
C42	0.4159	0.4286	0.4288	0.007391	0.424433	2.86116	2.01614	60.48419	0.047304
C52	0.479	0.475	0.4642	0.007656	0.472733	3.189776	1.687524	50.62571	0.063007

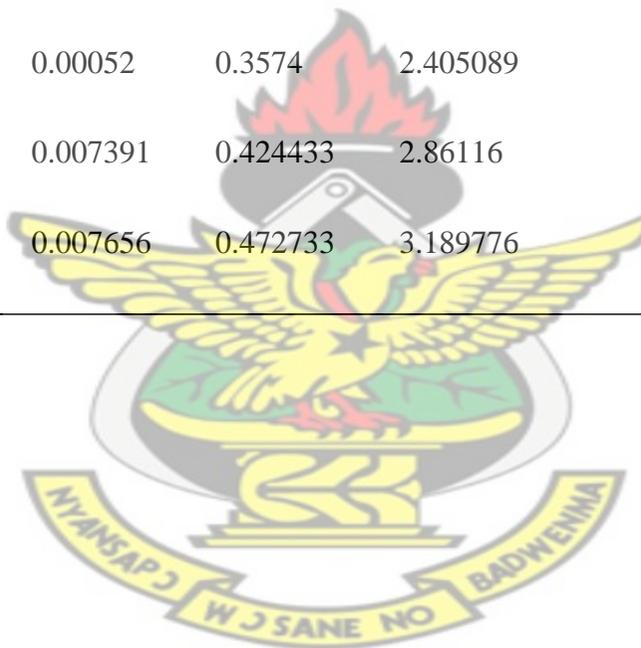


Table B.2, Concentration prepared = 8 mg/L

Actual concentration = 7.0927 mg/L

sample	A	B	average	eqm conc	ads conc	ads mass	C/X
A20	0.2506	0.252	0.2513	3.456807	3.635893	109.0768	0.031691
A40	0.2266	0.2273	0.22695	3.123975	3.968725	119.0618	0.026238
A50	0.266	0.2655	0.26575	3.654319	3.438381	103.1514	0.035427
A60	0.2531	0.2542	0.25365	3.488928	3.603772	108.1131	0.032271
A21	0.2122	0.2133	0.21275	2.92988	4.16282	124.8846	0.023461
A41	0.2491	0.251	0.25005	3.439721	3.652979	109.5894	0.031387
A51	0.231	0.2319	0.23145	3.185484	3.907216	117.2165	0.027176
A61	0.2883	0.2886	0.28845	3.964598	3.128102	93.84306	0.042247
A22	0.2089	0.2104	0.20965	2.887507	4.205193	126.1558	0.022888
A42	0.1758	0.1769	0.17635	2.43234	4.66036	139.8108	0.017397
A52	0.1587	0.1592	0.15895	2.194505	4.898195	146.9458	0.014934
A62	0.2331	0.2372	0.23515	3.236058	3.856642	115.6993	0.02797
B10	0.34	0.392	0.366	5.024604	2.068096	62.04289	0.080986
B30	0.2321	0.234	0.23305	3.207354	3.885346	116.5604	0.027517
B40	0.33	0.3378	0.3339	4.585839	2.506861	75.20582	0.060977
B50	0.3283	0.324	0.3262	4.48059	2.61211	78.36329	0.057177
B11	0.3205	0.3209	0.3285	4.512028	2.580672	77.42015	0.05828
B31	0.059	0.0596	0.0593	0.832422	6.260278	187.8083	0.004432
B41	0.2908	0.2913	0.29105	4.000137	3.092563	92.7769	0.043116
B51	0.3198	0.3204	0.3201	4.397212	2.695488	80.86465	0.054377
B12	0.3304	0.3301	0.3318	4.557135	2.535565	76.06695	0.05991
B32	0.2145	0.2127	0.2136	2.941498	4.151202	124.5361	0.02362

B42	0.2661	0.2684	0.26725	3.674822	3.417878	102.5363	0.035839
B52	0.3324	0.3331	0.33275	4.57012	2.52258	75.67739	0.06039
C10	0.4166	0.4193	0.41795	5.734691	2.294309	68.82927	0.083318
C20	0.4004	0.4041	0.40225	5.520093	2.508907	75.26721	0.07334
C40	0.4385	0.4419	0.4402	6.038819	1.990181	59.70543	0.101144
C50	0.4603	0.4523	0.4563	6.258885	1.770115	53.10346	0.117862
C11	0.4007	0.4024	0.40155	5.510525	2.518475	75.55425	0.072935
C21	0.4011	0.4027	0.4019	5.515309	2.513691	75.41073	0.073137
C41	0.4242	0.425	0.4246	5.825588	2.203412	66.10237	0.08813
C51	0.4373	0.4385	0.4379	6.007381	2.021619	60.64857	0.099052
C12	0.3932	0.3949	0.39405	5.40801	2.62099	78.6297	0.068778
C22	0.3986	0.3995	0.39905	5.476353	2.552647	76.5794	0.071512
C42	0.4202	0.4106	0.4154	5.699836	2.329164	69.87492	0.081572
C52	0.453	0.4528	0.4529	6.212411	1.816589	54.49767	0.113994

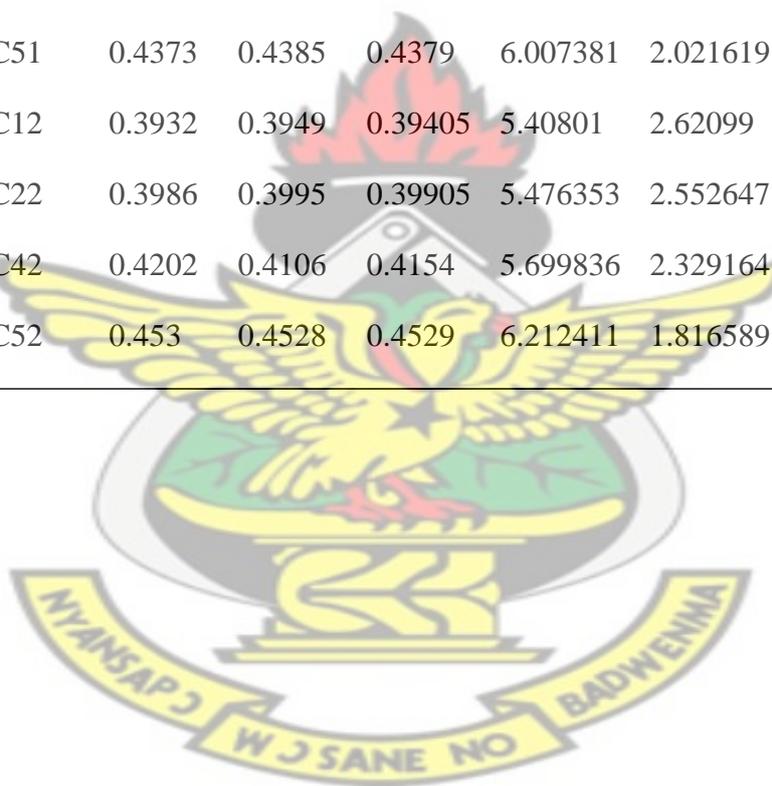


Table B.3 Concentration prepared = 10 mg/L

Actual concentration = 8.2478 mg/L

sample	A	B	C	std dev	average	eqm conc	conc ads	mass ads	C/X
						C (ug/ml)		ug/g X	
A20	0.6636	0.6636	0.663	0.000346	0.6634	4.544833	3.702967	111.089	0.040912
A40	0.6549	0.6717	0.6468	0.012701	0.6578	4.506561	3.741239	112.2372	0.040152
A50	0.6702	0.6756	0.6602	0.007814	0.668667	4.580827	3.666973	110.0092	0.04164
A60	0.6	0.61	0.62	0.01	0.61	4.17988	4.06792	122.0376	0.034251
A21	0.5736	0.5702	0.5689	0.002427	0.5709	3.912657	4.335143	130.0543	0.030085
A41	0.6264	0.6267	0.6489	0.012905	0.634	4.343904	3.903896	117.1169	0.03709
A51	0.599	0.5713	0.5914	0.014312	0.587233	4.024285	4.223515	126.7055	0.031761
A61	0.683	0.69	0.694	0.005568	0.689	4.719792	3.528008	105.8402	0.044594
A22	0.5138	0.5165	0.5138	0.001559	0.5147	3.528568	4.719232	141.577	0.024923
A42	0.4987	0.5026	0.5036	0.002589	0.501633	3.439266	4.808534	144.256	0.023841

A52	0.4259	0.4545	0.4326	0.014958	0.437667	3.002096	5.245704	157.3711	0.019077
A62	0.5638	0.575	0.5734	0.006058	0.570733	3.911518	4.336282	130.0885	0.030068
B10	0.9058	0.908	0.9026	0.002715	0.905467	6.199198	2.115502	63.46506	0.097679
B30	0.5644	0.576	0.5644	0.006697	0.568267	3.89466	4.42004	132.6012	0.029371
B40	0.7828	0.7838	0.8838	0.058026	0.8168	5.59322	2.72148	81.64439	0.068507
B50	0.7988	0.7938	0.7967	0.002511	0.796433	5.454028	2.860672	85.82017	0.063552
B11	0.7691	0.7732	0.7944	0.013579	0.7789	5.334199	2.980501	89.41503	0.059657
B31	0.1773	0.1915	0.1937	0.008902	0.1875	1.292373	7.022327	210.6698	0.006135
B41	0.7257	0.7232	0.729	0.002909	0.725967	4.972435	3.342265	100.268	0.049591
B51	0.7757	0.7734	0.7986	0.013933	0.782567	5.359258	2.955442	88.66325	0.060445
B12	0.8043	0.7925	0.7925	0.006813	0.796433	5.454028	2.860672	85.82017	0.063552
B32	0.5373	0.5273	0.5326	0.005003	0.5324	3.649535	4.665165	139.9549	0.026077
B42	0.6911	0.675	0.6899	0.008969	0.685333	4.694733	3.619967	108.599	0.04323
B52	0.7306	0.7463	0.738	0.007854	0.7383	5.056725	3.257975	97.73925	0.051737
C10	0.8796	0.8776	0.8774	0.001217	0.8782	6.012849	2.301851	69.05554	0.087073

C20	0.8321	0.8348	0.8358	0.001914	0.834233	5.712366	2.602334	78.07003	0.07317
C40	0.89	0.885	0.8819	0.004087	0.885633	6.06365	2.25105	67.53149	0.08979
C50	0.9439	0.9584	0.9546	0.007519	0.9523	6.519273	1.795427	53.86282	0.121035
C11	0.7936	0.7946	0.7926	0.001	0.7936	5.434664	2.880036	86.40109	0.0629
C21	0.8041	0.7998	0.8199	0.010584	0.807933	5.532623	2.782077	83.46232	0.066289
C41	0.8648	0.8648	0.89	0.014549	0.8732	5.978677	2.336023	70.08069	0.085311
C51	0.9592	0.9513	0.9529	0.004177	0.954467	6.534081	1.780619	53.41858	0.122318
C12	0.8468	0.8438	0.8468	0.001732	0.8458	5.791416	2.523284	75.69852	0.076506
C22	0.8258	0.8273	0.8281	0.001168	0.827067	5.663386	2.651314	79.53941	0.071202
C42	0.8632	0.8632	0.8692	0.003464	0.8652	5.924002	2.390698	71.72093	0.082598
C52	0.9324	0.9343	0.9403	0.004124	0.935667	6.405595	1.909105	57.27315	0.111843

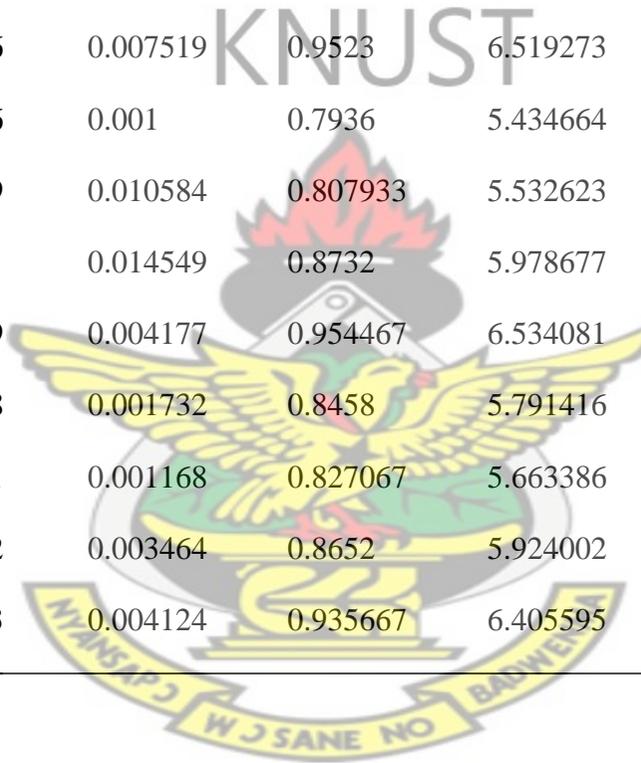


Table B.4 Concentration prepared = 15 mg/L

Actual concentration = 15.342 mg/L

Sample	A	B	C	std dev	average	eqm conc	conc ads µg/mL	mass ads	c/x
A20	0.2953	0.298	0.291	0.00353	0.294767	10.12735	5.214654	156.4396	0.064736
A40	0.2882	0.2847	0.2889	0.00225	0.287267	9.871059	5.470941	164.1282	0.060142
A50	0.2932	0.2921	0.2923	0.000586	0.292533	10.05103	5.29097	158.7291	0.063322
A60	0.2933	0.2963	0.301	0.003881	0.296867	10.19911	5.142893	154.2868	0.066105
A21	0.2961	0.2925	0.2864	0.004903	0.291667	10.02141	5.320586	159.6176	0.062784
A41	0.2754	0.2804	0.2727	0.003907	0.276167	9.491753	5.850247	175.5074	0.054082
A51	0.2942	0.3056	0.3027	0.005925	0.300833	10.33465	5.007345	150.2204	0.068797
A61	0.3023	0.298	0.298	0.002483	0.299433	10.28681	5.055186	151.6556	0.06783
A22	0.2795	0.2727	0.2771	0.003449	0.276433	9.500866	5.841134	175.234	0.054218
A42	0.2591	0.2569	0.2538	0.002663	0.2566	8.823127	6.518873	195.5662	0.045116

A52	0.2797	0.2665	0.2678	0.007275	0.271333	9.32659	6.01541	180.4623	0.051682
A62	0.2899	0.2884	0.2898	0.000839	0.289367	9.942819	5.399181	161.9754	0.061385
B10	0.3785	0.3798	0.3799	0.000781	0.3794	13.01941	2.62159	78.64771	0.165541
B30	0.2863	0.2816	0.2848	0.002401	0.284233	9.767405	5.873595	176.2079	0.055431
B40	0.3458	0.3456	0.34	0.003292	0.3438	11.8029	3.838102	115.1431	0.102506
B50	0.3403	0.3481	0.3423	0.004051	0.343567	11.79492	3.846076	115.3823	0.102225
B11	0.3506	0.3582	0.3511	0.004251	0.3533	12.12753	3.513471	105.4041	0.115057
B31	0.1014	0.0998	0.1003	0.000819	0.1005	3.488928	12.15207	364.5621	0.00957
B41	0.3258	0.3227	0.3258	0.00179	0.324767	11.1525	4.488503	134.6551	0.082823
B51	0.319	0.3316	0.33	0.00686	0.326867	11.22426	4.416743	132.5023	0.08471
B12	0.3462	0.3408	0.3408	0.003118	0.3426	11.76189	3.879108	116.3732	0.10107
B32	0.2933	0.2979	0.292	0.0031	0.2944	10.11482	5.526183	165.7855	0.061011
B42	0.2946	0.2979	0.2982	0.001997	0.2969	10.20025	5.440754	163.2226	0.062493
B52	0.311	0.3115	0.311	0.000289	0.311167	10.68776	4.953238	148.5971	0.071924
C10	0.3889	0.3875	0.3784	0.005701	0.384933	13.20849	2.432507	72.97522	0.181

C20	0.388	0.3722	0.37	0.009819	0.376733	12.92829	2.712715	81.38145	0.15886
C40	0.3778	0.3777	0.3788	0.000608	0.3781	12.97499	2.666014	79.98041	0.162227
C50	0.3909	0.3847	0.3996	0.007485	0.391733	13.44086	2.20014	66.00419	0.203636
C11	0.3614	0.3711	0.3674	0.004895	0.366633	12.58315	3.057849	91.73547	0.137168
C21	0.3592	0.3606	0.3653	0.003195	0.3617	12.41457	3.226429	96.79288	0.128259
C41	0.3795	0.373	0.373	0.003753	0.375167	12.87475	2.766251	82.98752	0.155141
C51	0.3899	0.3891	0.3895	0.0004	0.3895	13.36454	2.276457	68.2937	0.195692
C12	0.3729	0.3828	0.3841	0.006126	0.379933	13.03763	2.603366	78.10097	0.166933
C22	0.3603	0.3681	0.3852	0.012736	0.3712	12.7392	2.901798	87.05395	0.146337
C42	0.382	0.3974	0.3924	0.007856	0.3906	13.40213	2.238868	67.16603	0.199537
C52	0.3967	0.3906	0.40621	0.007867	0.397837	13.64942	1.991579	59.74736	0.228452

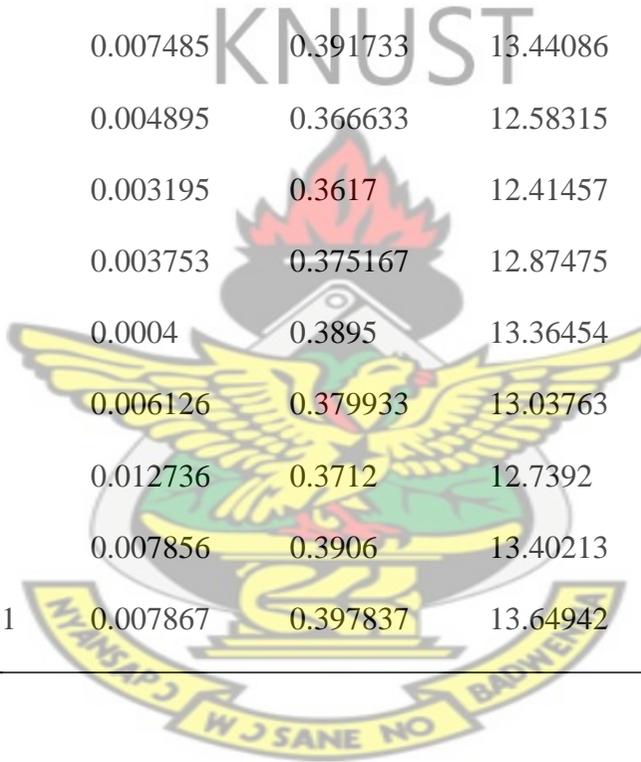
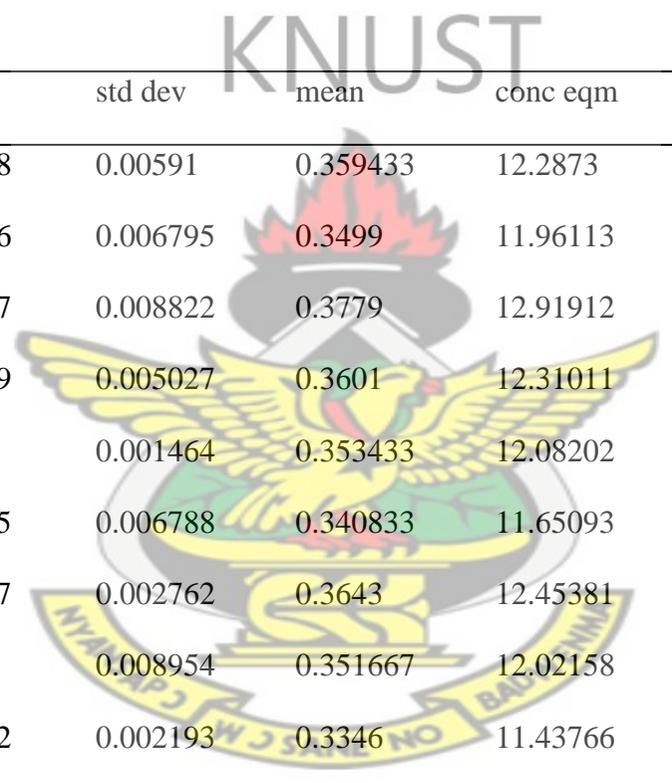


Table B.5 Concentration prepared = 20 mg/L

Actual concentration = 17.572 mg/L



Sample	A	B	C	std dev	mean	conc eqm	ads conc	mass ads	C/X
A20	0.3604	0.3531	0.3648	0.00591	0.359433	12.2873	5.284896	158.5469	0.0775
A40	0.3571	0.349	0.3436	0.006795	0.3499	11.96113	5.611067	168.332	0.071057
A50	0.388	0.374	0.3717	0.008822	0.3779	12.91912	4.653081	139.5924	0.092549
A60	0.3544	0.362	0.3639	0.005027	0.3601	12.31011	5.262086	157.8626	0.07798
A21	0.3521	0.3532	0.355	0.001464	0.353433	12.08202	5.490178	164.7053	0.073355
A41	0.34	0.348	0.3345	0.006788	0.340833	11.65093	5.921272	177.6381	0.065588
A51	0.364	0.3672	0.3617	0.002762	0.3643	12.45381	5.118389	153.5517	0.081105
A61	0.3422	0.3528	0.36	0.008954	0.351667	12.02158	5.550623	166.5187	0.072194
A22	0.3321	0.3355	0.3362	0.002193	0.3346	11.43766	6.134537	184.0361	0.062149
A42	0.334	0.3396	0.345	0.0055	0.339533	11.60645	5.96575	178.9725	0.06485
A52	0.3071	0.3134	0.3182	0.005567	0.3129	10.69522	6.876976	206.3093	0.051841

A62	0.3544	0.351	0.3544	0.001963	0.353267	12.07632	5.49588	164.8764	0.073245
B10	0.4376	0.4312	0.4394	0.00431	0.436067	14.90922	2.731781	81.95342	0.181923
B30	0.34	0.3408	0.355	0.008439	0.345267	11.80261	5.838391	175.1517	0.067385
B40	0.4	0.395	0.395	0.002887	0.396667	13.5612	4.079803	122.3941	0.110799
B50	0.4146	0.4146	0.4166	0.001155	0.415267	14.19757	3.443427	103.3028	0.137436
B11	0.4058	0.4085	0.4061	0.00148	0.4068	13.9079	3.733103	111.9931	0.124185
B31	0.1501	0.1525	0.1617	0.006123	0.154767	5.284887	12.35611	370.6834	0.014257
B41	0.3807	0.3845	0.3846	0.002223	0.383267	13.10273	4.538267	136.148	0.096239
B51	0.3881	0.3781	0.3758	0.006539	0.380667	13.01378	4.627223	138.8167	0.093748
B12	0.3909	0.3911	0.4017	0.006178	0.394567	13.48935	4.151652	124.5496	0.108305
B32	0.3515	0.3581	0.3522	0.003625	0.353933	12.09913	5.541871	166.2561	0.072774
B42	0.3529	0.3548	0.3584	0.002793	0.355367	12.14817	5.492832	164.7849	0.073721
B52	0.3755	0.3608	0.3648	0.0076	0.367033	12.54733	5.093671	152.8101	0.082111
C10	0.4452	0.4337	0.4357	0.006144	0.4382	14.98221	2.658791	79.76373	0.187832
C20	0.4381	0.4337	0.4308	0.003676	0.4342	14.84535	2.795646	83.86939	0.177006

C40	0.468	0.45	0.4682	0.010451	0.462067	15.79878	2.701223	81.03668	0.194958
C50	0.4787	0.4706	0.4728	0.004188	0.474033	16.2082	2.291798	68.75393	0.235742
C11	0.4441	0.453	0.4495	0.004484	0.448867	15.34716	3.152844	94.58533	0.162257
C21	0.4441	0.4414	0.4404	0.001914	0.441967	15.11108	3.388919	101.6676	0.148632
C41	0.4438	0.4681	0.4675	0.01386	0.4598	15.72123	2.778774	83.36321	0.188587
C51	0.4763	0.4633	0.4692	0.006509	0.4696	16.05652	2.443479	73.30437	0.219039
C12	0.4646	0.4569	0.4622	0.00394	0.461233	15.77027	2.729734	81.89202	0.192574
C22	0.4527	0.45	0.4522	0.001436	0.451633	15.44181	3.058186	91.74559	0.168311
C42	0.4681	0.4609	0.4629	0.003717	0.463967	15.86378	2.636216	79.08649	0.200588
C52	0.4814	0.482	0.475	0.00388	0.479467	16.3941	2.105903	63.17709	0.259494

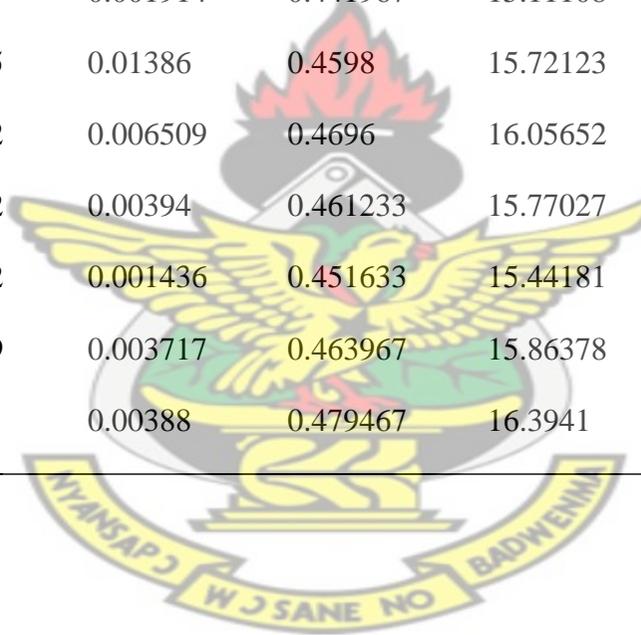
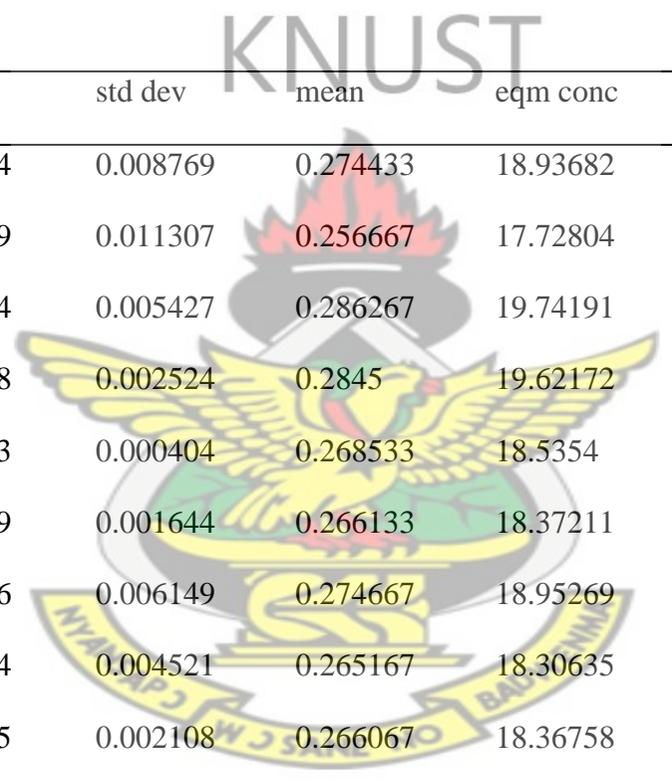


Table B.6 Concentration prepared = 25 mg/L

Actual concentration = 25.031 mg/L



Sample	A	B	C	std dev	mean	eqm conc	ads conc	ads mass	
A20	0.271	0.2679	0.2844	0.008769	0.274433	18.93682	6.093783	182.8135	0.103585
A40	0.247	0.2691	0.2539	0.011307	0.256667	17.72804	7.302564	219.0769	0.080922
A50	0.28	0.2894	0.2894	0.005427	0.286267	19.74191	5.288685	158.6606	0.124429
A60	0.2849	0.2868	0.2818	0.002524	0.2845	19.62172	5.408883	162.2665	0.120923
A21	0.2683	0.269	0.2683	0.000404	0.268533	18.5354	6.495198	194.856	0.095124
A41	0.2655	0.268	0.2649	0.001644	0.266133	18.37211	6.658486	199.7546	0.091973
A51	0.2776	0.2788	0.2676	0.006149	0.274667	18.95269	6.077908	182.3372	0.103943
A61	0.26	0.2671	0.2684	0.004521	0.265167	18.30635	6.724254	201.7276	0.090748
A22	0.2648	0.2649	0.2685	0.002108	0.266067	18.36758	6.663022	199.8906	0.091888
A42	0.2459	0.2423	0.2548	0.006435	0.247667	17.11571	7.914893	237.4468	0.072082
A52	0.2601	0.215	0.215	0.026038	0.230033	15.916	9.114602	273.4381	0.058207

A62	0.2645	0.2621	0.266	0.001967	0.2642	18.24058	6.790023	203.7007	0.089546
B10	0.3237	0.314	0.3151	0.005311	0.3176	21.87372	3.156876	94.70627	0.230964
B30	0.2723	0.271	0.2816	0.005781	0.274967	18.9731	6.057497	181.7249	0.104406
B40	0.2893	0.2834	0.2842	0.003201	0.285633	19.69883	5.331775	159.9532	0.123154
B50	0.2907	0.2952	0.2936	0.002281	0.293167	20.21137	4.819233	144.577	0.139797
B11	0.3095	0.3053	0.3062	0.002211	0.307	21.15254	3.878062	116.3419	0.181814
B31	0.0987	0.137	0.106	0.020335	0.1139	8.014696	17.0159	510.4771	0.0157
B41	0.2917	0.2756	0.2756	0.009295	0.280967	19.38132	5.649278	169.4783	0.114359
B51	0.2874	0.2995	0.2904	0.006301	0.292433	20.16147	4.869127	146.0738	0.138023
B12	0.3017	0.3127	0.2842	0.014373	0.299533	20.64453	4.386068	131.582	0.156895
B32	0.2863	0.2773	0.2615	0.012554	0.275033	18.97764	6.052961	181.5888	0.104509
B42	0.2709	0.2675	0.2702	0.001795	0.269533	18.60344	6.427162	192.8149	0.096483
B52	0.2867	0.297	0.2813	0.007976	0.288333	19.88252	5.148076	154.4423	0.128738
C10	0.3207	0.3272	0.3224	0.003371	0.323433	22.2706	2.759996	82.79989	0.268969
C20	0.3052	0.3252	0.3263	0.011877	0.3189	21.96217	3.068428	92.05285	0.238582

C40	0.3279	0.3279	0.3282	0.000173	0.328	22.5813	2.724696	81.74089	0.276255
C50	0.3191	0.327	0.338	0.009492	0.328033	22.58357	2.722429	81.67286	0.276513
C11	0.3138	0.3229	0.3184	0.00455	0.318367	21.92589	3.380114	101.4034	0.216224
C21	0.3136	0.3138	0.3138	0.000115	0.313733	21.61065	3.69535	110.8605	0.194936
C41	0.3159	0.3144	0.319	0.002346	0.316433	21.79435	3.511652	105.3495	0.206877
C51	0.3237	0.3287	0.324	0.002804	0.325467	22.40894	2.897055	86.91166	0.257836
C12	0.3299	0.3232	0.325	0.003467	0.326033	22.4475	2.858501	85.75504	0.261763
C22	0.3225	0.3126	0.3157	0.005064	0.316933	21.82837	3.477633	104.329	0.209226
C42	0.326	0.3243	0.3296	0.002706	0.326633	22.48832	2.81768	84.53039	0.266038
C52	0.3261	0.332	0.335	0.004528	0.331033	22.78768	2.518319	75.54957	0.301626

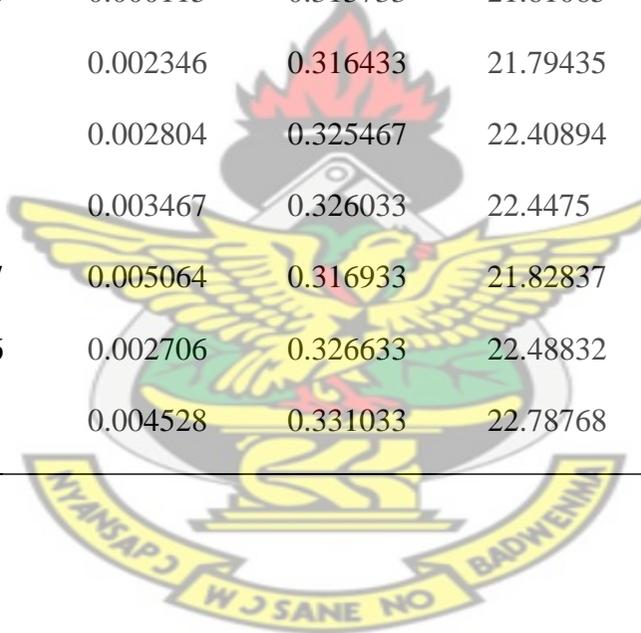
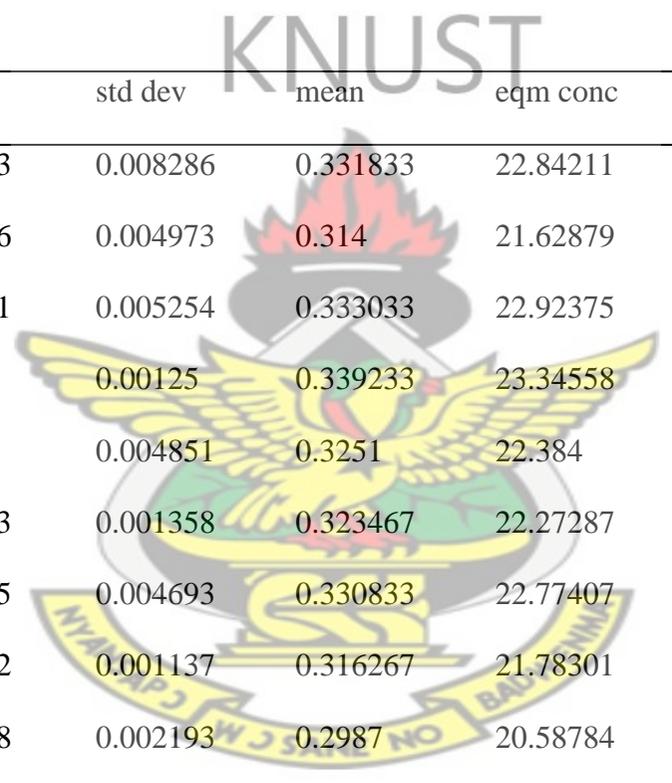


Table B.7 Concentration prepared = 30 mg/L

Actual concentration = 29.035 mg/L



sample	A	B	C	std dev	mean	eqm conc	conc ads	mass adso	C/X
A20	0.3359	0.3223	0.3373	0.008286	0.331833	22.84211	6.19249	185.7747	0.122956
A40	0.3123	0.3101	0.3196	0.004973	0.314	21.62879	7.405807	222.1742	0.097351
A50	0.33	0.33	0.3391	0.005254	0.333033	22.92375	6.110846	183.3254	0.125044
A60	0.3392	0.3405	0.338	0.00125	0.339233	23.34558	5.68902	170.6706	0.136787
A21	0.3203	0.325	0.33	0.004851	0.3251	22.384	6.650602	199.5181	0.11219
A41	0.3219	0.3242	0.3243	0.001358	0.323467	22.27287	6.761728	202.8519	0.109799
A51	0.3362	0.3288	0.3275	0.004693	0.330833	22.77407	6.260526	187.8158	0.121258
A61	0.3166	0.315	0.3172	0.001137	0.316267	21.78301	7.251591	217.5477	0.10013
A22	0.2982	0.3011	0.2968	0.002193	0.2987	20.58784	8.446765	253.4029	0.081245
A42	0.3118	0.3158	0.3184	0.003325	0.315333	21.71951	7.315092	219.4528	0.098971
A52	0.2786	0.2771	0.2878	0.005793	0.281167	19.39493	9.639671	289.1901	0.067066

A62	0.3214	0.3079	0.298	0.011746	0.3091	21.29541	7.739186	232.1756	0.091721
B10	0.391	0.3904	0.3904	0.000346	0.3906	26.84039	3.480114	104.4034	0.257083
B30	0.3426	0.3464	0.352	0.004729	0.347	23.874	6.446504	193.3951	0.123447
B40	0.3645	0.3646	0.358	0.003782	0.362367	24.91949	5.40101	162.0303	0.153795
B50	0.3684	0.372	0.371	0.001858	0.370467	25.47059	4.849914	145.4974	0.175059
B11	0.3867	0.3829	0.3891	0.003126	0.386233	26.54329	3.777206	113.3162	0.234241
B31	0.1779	0.1892	0.1889	0.006439	0.185333	12.87477	17.44573	523.372	0.0246
B41	0.3538	0.3412	0.3634	0.011134	0.3528	24.26861	6.051892	181.5568	0.13367
B51	0.3527	0.3624	0.3619	0.005462	0.359	24.69043	5.630066	168.902	0.146182
B12	0.368	0.3673	0.3772	0.005525	0.370833	25.49553	4.824968	144.749	0.176136
B32	0.3512	0.3543	0.3426	0.006062	0.349367	24.03502	6.285484	188.5645	0.127463
B42	0.3287	0.3287	0.3437	0.00866	0.3337	22.96911	7.351389	220.5417	0.104149
B52	0.3631	0.3576	0.3687	0.00555	0.363133	24.97165	5.348849	160.4655	0.15562
C10	0.3902	0.3985	0.4099	0.009891	0.399533	27.44818	2.872321	86.16963	0.318537
C20	0.3902	0.3837	0.3899	0.003669	0.387933	26.65896	3.661544	109.8463	0.242693

C40	0.4051	0.3863	0.3946	0.009421	0.395333	27.16243	3.158074	94.74223	0.286698
C50	0.3983	0.4011	0.3938	0.003683	0.397733	27.32571	2.994787	89.8436	0.304148
C11	0.3791	0.3836	0.3891	0.005008	0.383933	26.38681	3.93369	118.0107	0.223597
C21	0.3798	0.3824	0.3815	0.00132	0.381233	26.20311	4.117388	123.5217	0.212134
C41	0.3805	0.3825	0.3951	0.007915	0.386033	26.52969	3.790813	113.7244	0.233281
C51	0.3903	0.3943	0.3951	0.002572	0.393233	27.01955	3.300951	99.02853	0.272846
C12	0.3958	0.3932	0.3959	0.001531	0.394967	27.13748	3.183021	95.49063	0.28419
C22	0.3978	0.3952	0.3741	0.012998	0.389033	26.7338	3.586704	107.6011	0.248453
C42	0.4078	0.397	0.387	0.010403	0.397267	27.29396	3.026537	90.79611	0.300607
C52	0.4	0.4043	0.403	0.002205	0.402433	27.64548	2.675015	80.25046	0.34449

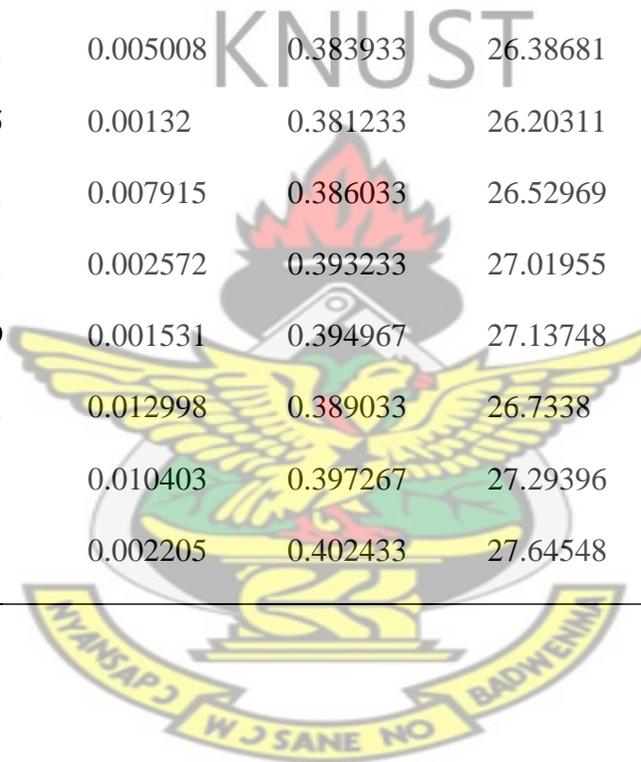
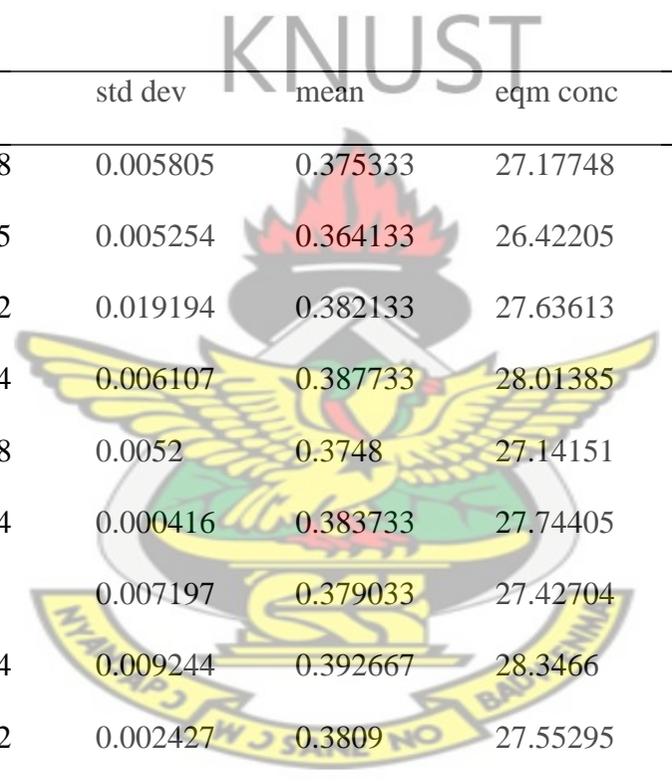


Table B.8 Concentration prepared = 35 mg/L

Actual concentration = 33.954 mg/L



sample	A	B	C	std dev	mean	eqm conc	conc ads	mass ads	C/X
A20	0.3773	0.3799	0.3688	0.005805	0.375333	27.17748	6.776419	203.2926	0.133687
A40	0.359	0.3639	0.3695	0.005254	0.364133	26.42205	7.531849	225.9555	0.116935
A50	0.36	0.3922	0.3942	0.019194	0.382133	27.63613	6.317765	189.533	0.145812
A60	0.394	0.3818	0.3874	0.006107	0.387733	28.01385	5.94005	178.2015	0.157203
A21	0.3716	0.372	0.3808	0.0052	0.3748	27.14151	6.812392	204.3718	0.132805
A41	0.3842	0.3836	0.3834	0.000416	0.383733	27.74405	6.209847	186.2954	0.148925
A51	0.373	0.3771	0.387	0.007197	0.379033	27.42704	6.526857	195.8057	0.140073
A61	0.4031	0.3855	0.3894	0.009244	0.392667	28.3466	5.607302	168.2191	0.16851
A22	0.3836	0.3789	0.3802	0.002427	0.3809	27.55295	6.400952	192.0286	0.143484
A42	0.3654	0.3655	0.3616	0.002223	0.364167	26.4243	7.5296	225.888	0.11698
A52	0.361	0.365	0.3798	0.009904	0.3686	26.72332	7.230576	216.9173	0.123196

A62	0.4008	0.3896	0.3755	0.012678	0.388633	28.07455	5.879346	176.3804	0.15917
B10	0.4185	0.418	0.42	0.001041	0.418833	30.11152	3.842384	115.2715	0.261222
B30	0.3755	0.378	0.3795	0.002021	0.377667	27.33486	6.619038	198.5711	0.137658
B40	0.3889	0.388	0.4	0.006684	0.3923	28.32187	5.632033	168.961	0.167624
B50	0.4048	0.4061	0.3968	0.005036	0.402567	29.01434	4.939556	148.1867	0.195796
B11	0.416	0.4171	0.4193	0.00168	0.417467	30.01934	3.934565	118.0369	0.254322
B31	0.1966	0.197	0.2051	0.004796	0.199567	15.32218	18.63172	558.9515	0.027412
B41	0.3816	0.3806	0.3938	0.007349	0.385333	27.85197	6.101928	183.0578	0.152148
B51	0.3508	0.3971	0.3996	0.027481	0.3825	27.66087	6.293034	188.791	0.146516
B12	0.4067	0.4035	0.3977	0.004562	0.402633	29.01884	4.935059	148.0518	0.196005
B32	0.3851	0.3724	0.3762	0.006518	0.3779	27.3506	6.6033	198.099	0.138065
B42	0.3671	0.3678	0.3618	0.003281	0.365567	26.51873	7.435172	223.0551	0.118889
B52	0.3913	0.3929	0.3951	0.001908	0.3931	28.37583	5.578074	167.3422	0.169568
C10	0.4291	0.444	0.426	0.009623	0.433033	31.06929	2.884607	86.53822	0.359024
C20	0.4137	0.4284	0.4137	0.008487	0.4186	30.09578	3.858122	115.7437	0.260021

C40	0.4244	0.43	0.4386	0.007153	0.431	30.93215	3.021754	90.65261	0.341216
C50	0.42	0.429	0.4405	0.010275	0.429833	30.85346	3.100444	93.01333	0.33171
C11	0.4126	0.4143	0.4105	0.001904	0.412467	29.68209	4.27181	128.1543	0.231612
C21	0.4108	0.4127	0.415	0.002103	0.412833	29.70682	4.247079	127.4124	0.233155
C41	0.4139	0.4235	0.4144	0.005404	0.417267	30.00585	3.948054	118.4416	0.253339
C51	0.4256	0.4228	0.4196	0.003002	0.422667	30.37007	3.583829	107.5149	0.282473
C12	0.4296	0.4264	0.4165	0.00683	0.424167	30.47124	3.482656	104.4797	0.291648
C22	0.4199	0.4193	0.4185	0.000702	0.419233	30.1385	3.815405	114.4621	0.263305
C42	0.428	0.4288	0.434	0.003258	0.430267	30.88268	3.071216	92.13649	0.335184
C52	0.4254	0.4375	0.4375	0.006986	0.433467	31.09852	2.855379	85.66138	0.36304

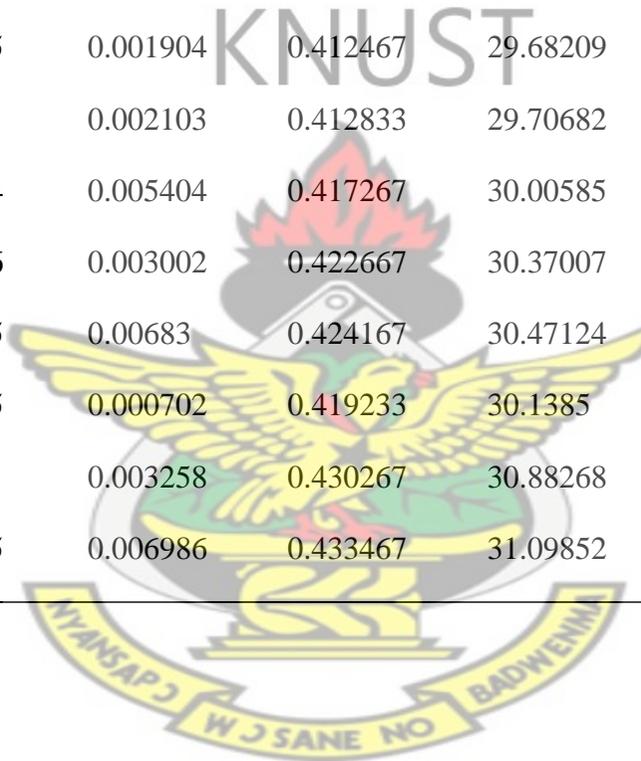
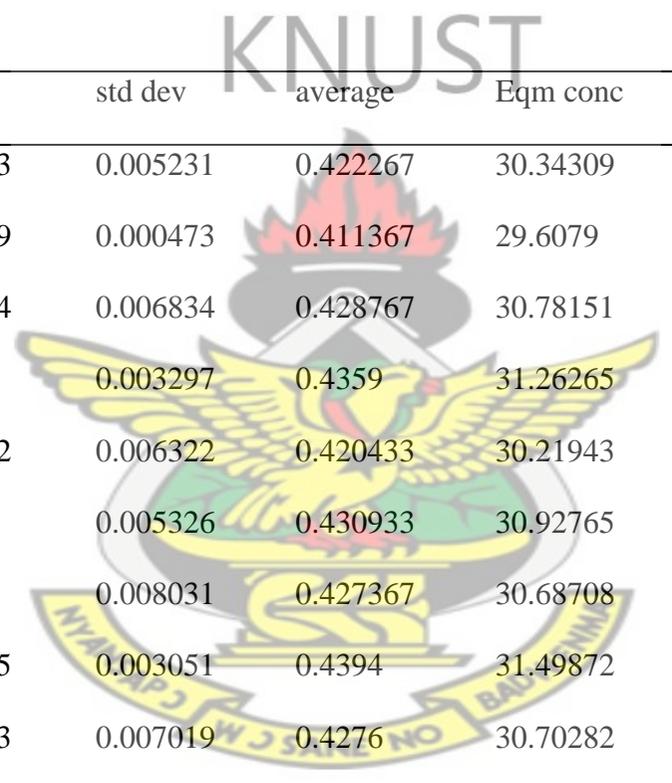


Table B.9 Concentration prepared = 40 mg/L

Actual concentration = 37.266 mg/L



sample	A	B	C	std dev	average	Eqm conc	conc ads	mass ads	C/X
A20	0.419	0.4195	0.4283	0.005231	0.422267	30.34309	6.922509	207.6753	0.146108
A40	0.4112	0.411	0.4119	0.000473	0.411367	29.6079	7.657704	229.7311	0.128881
A50	0.4349	0.43	0.4214	0.006834	0.428767	30.78151	6.48409	194.5227	0.158241
A60	0.4376	0.4321	0.438	0.003297	0.4359	31.26265	6.002953	180.0886	0.173596
A21	0.4132	0.4249	0.4232	0.006322	0.420433	30.21943	7.046166	211.385	0.142959
A41	0.4325	0.4353	0.425	0.005326	0.430933	30.92765	6.33795	190.1385	0.162659
A51	0.4235	0.4366	0.422	0.008031	0.427367	30.68708	6.578519	197.3556	0.155491
A61	0.4364	0.4393	0.4425	0.003051	0.4394	31.49872	5.766882	173.0064	0.182067
A22	0.4203	0.4282	0.4343	0.007019	0.4276	30.70282	6.562781	196.8834	0.155944
A42	0.4147	0.4137	0.4067	0.004359	0.4117	29.63038	7.635221	229.0566	0.129358
A52	0.4149	0.4115	0.4247	0.006854	0.417033	29.99011	7.275493	218.2648	0.137402

A62	0.4215	0.4313	0.4383	0.008439	0.430367	30.88943	6.376172	191.2851	0.161484
B10	0.4591	0.4633	0.4747	0.008072	0.4657	33.27263	3.992971	119.7891	0.27776
B30	0.4294	0.4234	0.4234	0.003464	0.4254	30.55443	6.711169	201.3351	0.151759
B40	0.4399	0.4309	0.4399	0.005196	0.4369	31.3301	5.935504	178.0651	0.175947
B50	0.4562	0.4481	0.4407	0.007753	0.448333	32.10126	5.164336	154.9301	0.207198
B11	0.4602	0.4659	0.4646	0.002987	0.463567	33.12874	4.136862	124.1059	0.266939
B31	0.246	0.2458	0.2423	0.002081	0.2447	18.36638	18.89922	566.9765	0.032394
B41	0.4394	0.4221	0.4364	0.009245	0.432633	31.04231	6.223287	186.6986	0.16627
B51	0.4225	0.4249	0.4333	0.005671	0.4269	30.65561	6.609995	198.2998	0.154592
B12	0.4432	0.4494	0.4576	0.007223	0.450067	32.21818	5.047425	151.4227	0.21277
B32	0.427	0.4305	0.4203	0.005183	0.425933	30.5904	6.675196	200.2559	0.152757
B42	0.4151	0.4126	0.4105	0.002303	0.412733	29.70008	7.565524	226.9657	0.130857
B52	0.4332	0.44	0.4496	0.00824	0.440933	31.60214	5.66346	169.9038	0.186
C10	0.4789	0.4815	0.482	0.001664	0.4808	34.29111	2.97449	89.23469	0.38428
C20	0.468	0.4691	0.4686	0.000551	0.468567	33.46598	3.799617	113.9885	0.293591

C40	0.4677	0.4876	0.4849	0.010795	0.480067	34.24165	3.023952	90.71857	0.377449
C50	0.4721	0.4751	0.4824	0.005297	0.476533	34.00333	3.262273	97.86818	0.34744
C11	0.4551	0.4651	0.4614	0.005056	0.460533	32.92414	4.341458	130.2437	0.252789
C21	0.4601	0.456	0.466	0.005027	0.4607	32.93538	4.330216	129.9065	0.253531
C41	0.4636	0.4644	0.4736	0.005557	0.4672	33.3738	3.891797	116.7539	0.285847
C51	0.4635	0.4696	0.4649	0.003195	0.466	33.29286	3.972736	119.1821	0.279345
C12	0.48	0.466	0.468	0.007572	0.471333	33.65259	3.613008	108.3902	0.310476
C22	0.4681	0.4621	0.4652	0.003001	0.465133	33.23441	4.031192	120.9358	0.27481
C42	0.4757	0.4781	0.4759	0.001332	0.476567	34.00558	3.260024	97.80073	0.347703
C52	0.4791	0.4835	0.4813	0.0022	0.4813	34.32483	2.940765	88.22296	0.389069

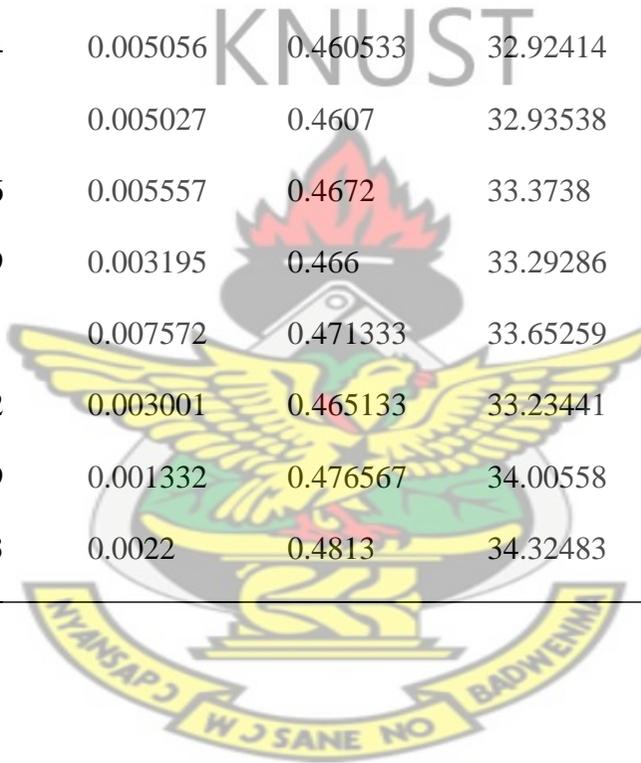
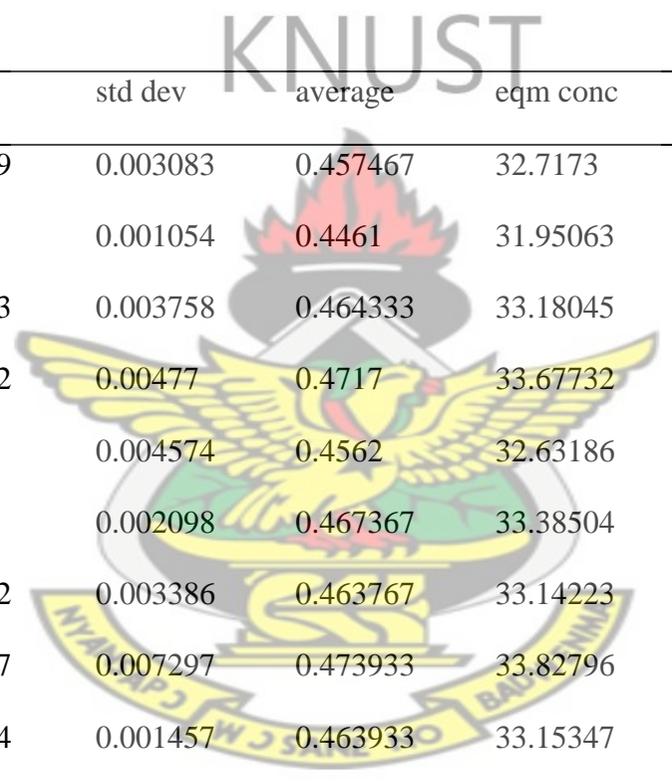


Table B.10 Concentration prepared = 45 mg/L

Actual concentration = 37.266 mg/L



sample	A	B	C	std dev	average	eqm conc	ads conc	mass ads	C/X
A20	0.454	0.4585	0.4599	0.003083	0.457467	32.7173	7.070702	212.121	0.154239
A40	0.4471	0.4462	0.445	0.001054	0.4461	31.95063	7.837373	235.1212	0.13589
A50	0.46	0.4667	0.4663	0.003758	0.464333	33.18045	6.607551	198.2265	0.167387
A60	0.4747	0.4742	0.4662	0.00477	0.4717	33.67732	6.110676	183.3203	0.183708
A21	0.4596	0.458	0.451	0.004574	0.4562	32.63186	7.156137	214.6841	0.151999
A41	0.4681	0.465	0.469	0.002098	0.467367	33.38504	6.402956	192.0887	0.1738
A51	0.4652	0.4599	0.4662	0.003386	0.463767	33.14223	6.645772	199.3732	0.166232
A61	0.4765	0.4796	0.4657	0.007297	0.473933	33.82796	5.96004	178.8012	0.189193
A22	0.4651	0.4623	0.4644	0.001457	0.463933	33.15347	6.634531	199.0359	0.16657
A42	0.4521	0.4458	0.4452	0.003822	0.4477	32.05855	7.729454	231.8836	0.138253
A52	0.458	0.4514	0.4514	0.003811	0.4536	32.4565	7.331505	219.9451	0.147566

A62	0.4671	0.4663	0.4639	0.001665	0.465767	33.27713	6.510874	195.3262	0.170367
B10	0.5038	0.5039	0.5006	0.001877	0.502767	35.77274	4.015258	120.4578	0.296973
B30	0.4645	0.466	0.4513	0.008089	0.4606	32.92864	6.859361	205.7808	0.160018
B40	0.47	0.47	0.476	0.003464	0.472	33.69756	6.090442	182.7132	0.184429
B50	0.4827	0.4845	0.4816	0.001464	0.482933	34.435	5.352998	160.59	0.214428
B11	0.4927	0.4969	0.5084	0.008128	0.499333	35.54117	4.246834	127.405	0.278962
B31	0.2821	0.2834	0.27	0.00739	0.2785	20.64616	19.14184	574.2551	0.035953
B41	0.4638	0.465	0.4754	0.006379	0.468067	33.43226	6.355741	190.6722	0.175339
B51	0.4551	0.4541	0.4766	0.012712	0.461933	33.01857	6.769429	203.0829	0.162587
B12	0.4859	0.481	0.4907	0.00485	0.485867	34.63285	5.155148	154.6544	0.223937
B32	0.4605	0.463	0.4601	0.001572	0.4612	32.96911	6.818892	204.5668	0.161166
B42	0.4492	0.4415	0.4568	0.00765	0.449167	32.15747	7.630529	228.9159	0.140477
B52	0.4757	0.476	0.4799	0.002343	0.4772	34.04829	5.739706	172.1912	0.197735
C10	0.518	0.5143	0.5165	0.001861	0.516267	36.6833	3.104696	93.14088	0.393848
C20	0.503	0.5024	0.508	0.003075	0.504467	35.88741	3.900595	117.0178	0.306683

C40	0.5185	0.5191	0.51	0.00509	0.515867	36.65632	3.131676	93.95027	0.390167
C50	0.4957	0.5192	0.5262	0.015977	0.5137	36.51018	3.277815	98.33446	0.371286
C11	0.5012	0.4951	0.4914	0.004949	0.4959	35.30959	4.478409	134.3523	0.262814
C21	0.4901	0.499	0.501	0.005803	0.4967	35.36355	4.424449	132.7335	0.266425
C41	0.5021	0.5029	0.5019	0.000529	0.5023	35.74127	4.046735	121.402	0.294404
C51	0.5188	0.498	0.5008	0.011288	0.505867	35.98183	3.806166	114.185	0.315119
C12	0.5039	0.5099	0.5077	0.003035	0.507167	36.06952	3.718482	111.5545	0.323335
C22	0.4953	0.4973	0.5132	0.009808	0.501933	35.71653	4.071466	122.144	0.292413
C42	0.5103	0.5153	0.512	0.002542	0.512533	36.43149	3.356506	100.6952	0.3618
C52	0.5194	0.5184	0.5174	0.001	0.5184	36.8272	2.960805	88.82414	0.414608

