

**KINETICS OF SULPHATE DESORPTION IN SELECTED SOILS AS  
INFLUENCED BY PARENT MATERIALS AND BIOCHAR IN BAUCHI  
NORTH, SUDAN SAVANNA, NIGERIA**

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FACULTY OF AGRICULTURE,  
AHMADU BELLO UNIVERSITY ZARIA  
NIGERIA**

**AUGUST, 2018**

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SOIL SCIENCE) IN THE DEPARTMENT OF SOIL SCIENCE, FACULTY  
OF AGRICULTURE, AHMADU BELLO UNIVERSITY ZARIA, NIGERIA**

**AUGUST, 2018**

## **DECLARATION**

I hereby declare that this dissertation was written by me and it is a record of my M.Sc work. It has not been presented before as any degree research work at any university. References made to published literature have been duly acknowledged.

**ALIYU, Murabbi**

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Signature

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Date

## CERTIFICATION

This dissertation titled “Kinetics of sulphate desorption of selected soils as influenced by parent materials and biochar in Sudan savanna Nigeria” by Aliyu Murabbi meets the requirement for the award of Master of Science degree of Ahmadu Bello university, Zaria and is approved for its valuable contribution to knowledge and literary presentation.

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## **DEDICATION**

I dedicate this dissertation solely to my parents, Alhaji Aliyu Tamasini and Sadiya Kabir and also to my wife Zainab Yahaya and my son Abdurrahman Murabbi.

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## ABSTRACT

The absorptive nature of S by plants depends on desorption of S from soils. Understanding the kinetics desorption of sulphate as influenced by parent materials and biochar is critical for effective precision of S diagnosis and fertilization recommendations to ensure sustainable and profitable crop production and environmental protection. In this study, soils derived from three (3) different parent materials namely; Chad formation (CF), Basement complex rock (BCR) and Kerri-Kerri formation (KKF) in the Sudan savanna and biochar soils were investigated on the kinetics of sulphate desorption behaviour. In the desorption experiment, soils were allowed to adsorb sulphate as in the adsorption studies and the adsorbed sulphate was extracted by shaking for 30, 60, 150, 180 and 240 minutes with 15 ml  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  solution containing 500 mg P L<sup>-1</sup> respectively. Five kinetic models first-order, second-order, Elovich, fractional power and parabolic diffusion models were used to test best model for describing S desorption in the soils of varying parent materials. Results indicated that the mean values of both soil pH in water and  $\text{CaCl}_2$  were significantly ( $p>0.05$ ) different between soil parent materials. The soils are low in organic carbon (range; 2.90 to 7.25 g/kg) in all the studied soils. The mean values of exchangeable bases and CEC were not significantly ( $p>0.05$ ) different by soil parent materials. The mean values of the different forms of oxides were significantly different ( $p>0.05$ ) by soil parent materials. The mean values of total sulphur and organic in all soils from three parent materials were significantly different ( $p > 0.05$ ). The values of inorganic sulphur (Org.S) ranged from 18.33 to 123.78 mg/kg in all the soils across three parent materials, however the mean values were not significantly different ( $p>0.05$ ). The results revealed that sulphate desorption decreased with increasing shaking time (range; 34.96 to 19.09 mg/kg) in all the studied soils. Rate of desorption was also characterized by an initial rapid desorption with > 65% being desorbed in the first 30 minutes which was considered as good index for describing S desorption maximum followed by a slow release that progressed gradually up to 240 minutes. The adsorption-desorption processes were irreversible and hysteretic in nature. The trend of magnitude of rate of desorption by the soil parent materials was in descending order: CF>BCR>KKF. The study showed that the parabolic diffusion and first-order models were found to describe S desorption data satisfactorily as characterized by relatively high R<sup>2</sup> values and lowest S.E values by soil parent materials, respectively. Comparison of R<sup>2</sup> values of the best isotherm equations indicated that both Langmuir and Freundlich isotherm models were suitable to describe S desorption data in all the studied soils, as can be seen from R<sup>2</sup> greater than 0.98. However, in view of the low SE, Langmuir equation gave a better fit to experimental data in this study. Organic matter had a significant influence on modeling of S desorption in these soils. The results also revealed that the BC used in this study did not have significant effect on release of adsorb S ( $p>0.05$ ). Based on the results, can be concluded that rate of sulphate desorption by these soils are time-dependent and mainly controlled by diffusion-controlled phenomena. It is recommended that sulphur management practice in the farm should be tied up with OM management. It is also recommended that affinity of BC to release plant nutrients should be tested before applying to soils as amendment.

## CHAPTER ONE

### 1.0 Introduction

The essentiality of sulphur (S) for plant growth has been known from the time of Liebig (Tabatabai, 2005a), but compared with other major nutrients such as nitrogen (N), phosphorus (P) and potassium (K) it has, until recently, received little attention. Plant adsorb sulphate ( $\text{SO}_4^{2-}$ ) from the soil solution, therefore replenishment from organic and adsorbed sources is important in maintaining sulphate supply to the plant (Sumner, 2000).

Importance of S as a plant nutrient was largely overlooked in soil science research, mainly because the incidental supply of S via deposition and S- containing N and P fertilizer was usually sufficient to meet crop demands. However, since concerns about intensive continuous cropping were adopted among farmers in the decades, sulphur stock has decreased remarkably in some soils in the world. In the 1980s, issues of acid rains were raised in Nigeria (Osu *et al.*, 2013), and sulphur emission from power plants and industries has significantly declined which has led to major causes of S deficiency in some soils.

Over the last 2 decades, farmers deviate from using sulphur rich fertilizers to high analysis fertilizers that contain less amount of sulphur which has masked many latent or incipient sulphur deficiencies in cultivated land in Nigeria (Raji, 2008). The reduced input of S combined with intensified farming and larger S removal in harvests depleted the S stocks in soils and in the 1990s, sulphur deficiency began to surface (Ceccotti, 1996).

Sulphur deficiency can cause marked yield loss and reduce the quality of crops and forage in some soils of the world (Wang *et al.*, 2002; 2008; Zhao *et al.*, 2006a). In addition, S deficiency



decreases resistance to pathogens (Falk *et al.*, 2007; Walters and Bingham, 2007) and reduces N utilization efficiency (Ahmad and Abdin, 2000).

## **1.1 Problem statement**

As sulphur is relatively cheap element, fertilization with S is now becoming standard practice (Boye, 2011). However, knowledge of how to optimize the amount and timing of S fertilization is still insufficient. Sulphur fertilization can decrease selenium (Se) content in crops, which is problematic for animal and human nutrition in Se-poor soils (Stroud *et al.*, 2010). Sulphur can also induce eutrophication in freshwater wetlands, as the precipitation of iron-sulphide releases iron-bonded phosphates (Lamers *et al.*, 2002), the understanding of the kinetics of  $\text{SO}_4^{2-}$  desorption is critical in preventing such problems.

Sulphur is widely distributed in nature in both, organic and inorganic forms. Inorganic S is in the readily available fraction for root uptake, or may be adsorbed on to soil colloids, but represents an average of less than 5% of total S in the soil. The majority of S (> 95%) in soil is bound to organic molecules and is only indirectly available to plants (Kertesz and Mirleau, 2004). In Nigeria, savanna soils cover an extensive land mass that support agrarian activities (Abubakar, 2007). Basically these soils are well drained and acidic with low cation exchange capacity and organic matter content and have mixed or kaolinitic clay fraction enriched with sesquioxides (Abdu, 2006). Each of these parameters could affect the kinetics of sulphate desorption from soils. Variable charges are also major component of most soil in the tropics that make S unavailable to plants. Such is the case with Nigerian soils that are highly weathered. In general, soils that contain higher quantities of Fe and Al oxides will have greater sulphate adsorption capacities.

## 1.2 Justification of the study

The kinetics of  $\text{SO}_4^{2-}$  desorption and its sorption is important for describing, studying and managing S status in soils. Various adsorption studies suggest that sulphate might be held in various soil fractions each having unique retention sites and energy of each retention site will add in predicting the desorption and release of soil  $\text{SO}_4^{2-}$  and in describing chemical and physical procedures that enhance sulphate removal (Brajendra *et al.*, 2013). Therefore, the interest in  $\text{SO}_4^{2-}$  is to determine its fate and efficiency of native and applied  $\text{SO}_4^{2-}$  into the soil with time. In addition, the kinetics of sulphate desorption is also very important in agronomic practice as P for the release of ions to plants and also allows them to leach and contaminate the ground water (Garg *et al.*, 2016).

Numerous excellent studies are available on sulphate adsorption (Alves and Lavorenti, 2004; Osodeke *et al.*, 2006; Jung *et al.*, 2011; Uzoho *et al.*, 2014; Farahmand *et al.*, 2015), and few research has been undertaken on sulphate desorption in soils. However, overwhelming majority of such studies in the world and in Nigeria in particular has been done on P with very little attention given to sulphate. Several mathematical models have been used to describe adsorption/desorption data of nutrient elements such as P (Abdu, 2006) and  $\text{SO}_4^{2-}$ . Modeling of desorption data is essential for characterizing release of adsorbed sulphate by soil, and this enhances the predictability of the optimum quantity of sulphate fertilizer to apply to such a soil for optimal crop growth and yield as well as environment protection.

Biochar when used as a soil amendment, has been reported to boost soil fertility (Sohi *et al.*, 2012) and improve soil quality by raising soil pH, increasing moisture holding capacity, attracting more beneficial fungi and microbes, improving cation exchange capacity (CEC), and

increasing nutrient sorption efficiency in soil (Lehmann *et al.*, 2006; Rondon *et al.*, 2006; Lehmann, 2007). Another major benefit associated with the use of biochar as a soil amendment is its ability to sequester carbon from the atmosphere-biosphere pool and transfer it to soil (Lehmann and Joseph 2009; Laird, 2010) and it may persist in soil for long period of time because it is very resistant to microbial decomposition and mineralization. This particular characteristic of biochar depends strongly on its properties, which is affected in turn by the pyrolysis conditions and the type of feedstock used in its production. Unfortunately, little data are available in the literature for effect of biochar on kinetics desorption of sulphate by soils.

Therefore, the period of contact with the soil matrix / solution is another important component which determines the rate at which the sulphate desorption can take place and in turn get assimilated by plants or becomes prone to leaching. The chemistry of sulphate desorption is thus essential in understanding the chemical behaviour of sulphate ion and in formulating the fertilizer schedule for raising optimum crop production in view of the low recovery of this ion by most of the agricultural soils. This dissertation also could help advisers and growers to make better decision about S management in soils to ensure high sustainable soil productivity in the era of intensive agricultural practices and climate change as well as to minimize risks to environmental quality.

## **1.2 Objectives**

The broad objective of this research is to make a contribution towards more comprehensive description of the sulphate adsorption and release kinetics by soil as influenced by parent materials.

The specific objectives set for this work were to:

1. To assess the kinetics of sulphate desorption in selected soils of different parent materials of Bauchi North, Sudan Savanna of Nigeria.
2. To compare five (5) kinetic models (First-order, Second-order, Elovich, Fractional power and Parabolic diffusion models) for describing  $\text{SO}_4^{2-}$  desorption in the soils of varying parent materials in the Sudan savanna.
3. To determine the relationships between soil properties and models rate constant.
4. To determine the effect of biochar on sulphate sorption and release kinetics in the soil of different parent materials.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Sulphur

Sulphur (S) is unique in having gained relevance within past decades from an undesired pollutant to being seen as a major nutrient, limiting plant growth and yield (Barker and Pilbeam, 2007). It is the 13<sup>th</sup> most abundant element in the earth crust within an average content range of between 0.06-0.10% (Tabatabai, 2005b; Patel *et al.*, 2013a; Bappa *et al.*, 2014), and the second most abundant anion (Likens *et al.*, 2002; Yi-Balan, 2013) for plant growth and development. It is similar to N in its role and functions in plant production, is comparable to P in terms of overall crop needs, and could be equated with K in terms of per unit cost (Bappa *et al.*, 2014). All organisms need S for growth, primarily as a component of the amino acids cysteine and methionine, as part of several enzyme cofactors (including biotin, coenzyme A, coenzyme M, thiamine and lipoic acid), and as an essential participant in many redox reactions (Yi-Balan, 2013).

#### 2.2 Sources of sulphur in soils

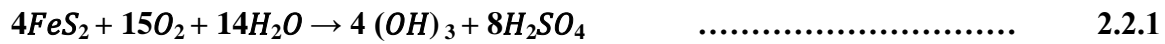
Sulphur in soils originates from 3 major sources. These sources are: parent material, organic and inorganic fertilizers and atmospheric deposition of sulphur gases (Tabatabai, 2005a; Fageria, 2009; Brady and Weil, 2013). Parent material is a major source of S in all types of soils and it ranges between 0.026-1.0 percent (Sabir *et al.*, 2015). Diverse parent materials contain varying amounts of S in the order: igneous rocks < metamorphic rocks < magmatic rocks << limestone < sedimentary rocks (sulphides) < shales < sedimentary rocks (sulphates) << coal (Bowen, 1966; Friend, 1973).

Many S-containing minerals occur in nature. The main S-bearing minerals in rocks and soils are present in 2 states: (1) as sulphate, such as in gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ),

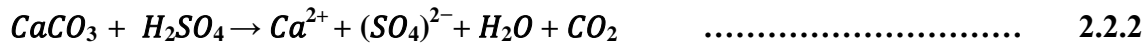
epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ); or (2) as sulfide, such as pyrite and marcasite ( $\text{FeS}_2$ ), sphalerite ( $\text{ZnS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), cobaltite ( $\text{CoAsS}$ ), pyrrhotite ( $\text{Fe}_{11}\text{S}_{12}$ ), galena ( $\text{PbS}$ ), arsenopyrite ( $\text{FeS}_2 \cdot \text{FeAs}_2$ ), and pentlandite ( $\text{Fe,Ni}_9\text{S}_8$ ) (Tabatabai, 2005a). Igneous rocks, such as pyrite ( $\text{FeS}_2$ ) consist of the original pool of S on earth (Sabir *et al.*, 2015). Gypsum and anhydrite are major constituents of many sedimentary rocks (Chikyala, 2007). Upon weathering S in pyrite undergoes oxidation to the sulphate form, which is assimilated by plants and micro-organisms (Ajwa, 1993).

Sulphate form of Sulphur can also occur as the result of the oxidation of pyrite in sedimentary rocks (equation 2.2.1), especially shale (Harris *et al.*, 2004; Freese, 2014). In pyrite bearing rocks the oxidation of pyrite results in the formation of acid sulphate (Freese, 2014) (Equation 2.2.2). Calcium also within these rocks reacts with the acid sulphate to form gypsum (Chikyala, 2007) (equation 2.2.3).

Oxidation of pyrite



Dissolution of calcite



Formation of gypsum



### 2.3 Forms of sulphur in soils

Sulphur is ubiquitous and presents a large variety of species and valence states from -2 (in sulphides) to + 6 (in sulphates) which in turn are assimilated by plants (Jalilehvand, 2006; Blum, 2012). Sulphur in tropical soils is present in both organic and inorganic forms, although, the organic form is dominant in most agricultural soils (Blum, 2012; Yi-Balan, 2013; Bappa *et al.*, 2014; Sabir *et al.*, 2015). More than 95% of the total S in most soils from humid and semi humid regions are organic sulphate (Tabatabai, 2005a). Inorganic sulphur generally accounts for less than 10% of total S in temperate soils (Fageria, 2009), and humid tropical soils (Solomon *et al.*, 2001).

In well-drained, aerated soils, most of the inorganic sulphur can be in the form of easily soluble fraction, adsorbed by soil colloids, insoluble or co-precipitated with  $\text{CaCO}_3$ . Under anoxic conditions inorganic S mostly exists as sulphide and elemental S (Tabatabai, 2005b; Conte, 2011). Being the mobile form, sulphate is readily available for plants, and also prone to be leached (Cichota, 2007). Sulphate also adsorbs, via various mechanisms (specific and non-specific) onto the soil particles. Leaching of sulphate and sulphate adsorption in soils are influenced by chemical and physical parameters such as clay type and content, hydrous oxides, the presence of cations and other anions, soil pH, sulphate concentration, temperature, soil depth and so on.

The adsorption is by ligand exchange with surface hydroxyl groups by which sulphate replaces  $\text{OH}^-$  coordinated to  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  to form a covalent bond with the surface (Mengel *et al.*, 2001) or by electrostatic attraction of sulphate ion for positive sites (Tabatabai, 2005a). Sulphate losses are reduced (i.e. adsorption is increased) by the presence of roots, Al and Fe oxides or by

increasing soil acidity (Tabatabai, 2005a; Conte, 2011). Adsorption of sulphate is usually negligible above soil pH 6.5 (Ajwa and Tabatabai, 1995b).

However, as for nitrogen, sulphur is mainly present in organic forms. Much of the organic sulphur in soils remains uncharacterized.

Thus, 3 distinct groups of S-containing compounds have been identified (Tabatabai, 2005a) as follows:

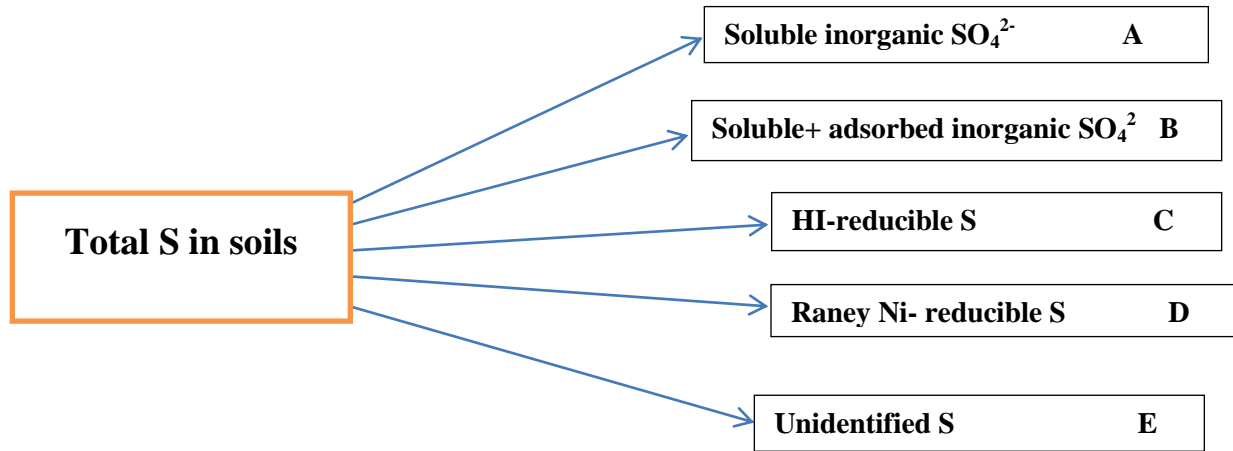
1. Organic S that is not directly bonded to C and is reduced to H<sub>2</sub>S by hydriodic acid (HI). This fraction is believed to be largely in the form of sulphate ester with C-O-S linkages. Examples of substances that contain these linkages include arylsulphate, alkylsulphates, phenolic sulphate, sulphamates (C-N-S), choline sulphate, and sulphated lipids and so on.
2. Organic S that is directly bonded to C (C-S) and is reduced to inorganic sulphide by Raney Ni (50% each of Ni and Al powder). This fraction is believed to consist largely of S in the form of S-containing amino acids such as methionine and cysteine.
3. Organic S that is not reduced by either of the reagents employed in estimation of fractions 1 and 2. This unidentified fraction is inert to HI and Raney Ni, and also is of little importance as a potential source of S for plants

Moreover, inside soil - plant system, 4 main types of biologically – mediated processes occur (Figure 2.2.): assimilation (conversion of inorganic S, usually sulphate into organic S by plants or microorganisms), mineralization (conversion of organic sulphur to sulphate), reduction (of sulphate to sulphide) and oxidation (of reduced S compounds to sulphate) (Yi-Balan, 2013).

In past decade, interest in soil chemistry-fertility related aspects of S cycle is increasing, as widespread crop deficiencies are reported with increasing frequency (Kost *et al.*, 2008; Scherer,



Figure 2.1. Summary of the classes of sulphur fractions in soils.



$$B - A = \text{Adsorbed } \text{SO}_4^{2-}$$

$$C - B = \text{Ester } \text{SO}_4^{2-}$$

$$\text{Total S} - (C + D) = E$$

$$\text{Total S} - B = \text{Organic S}$$

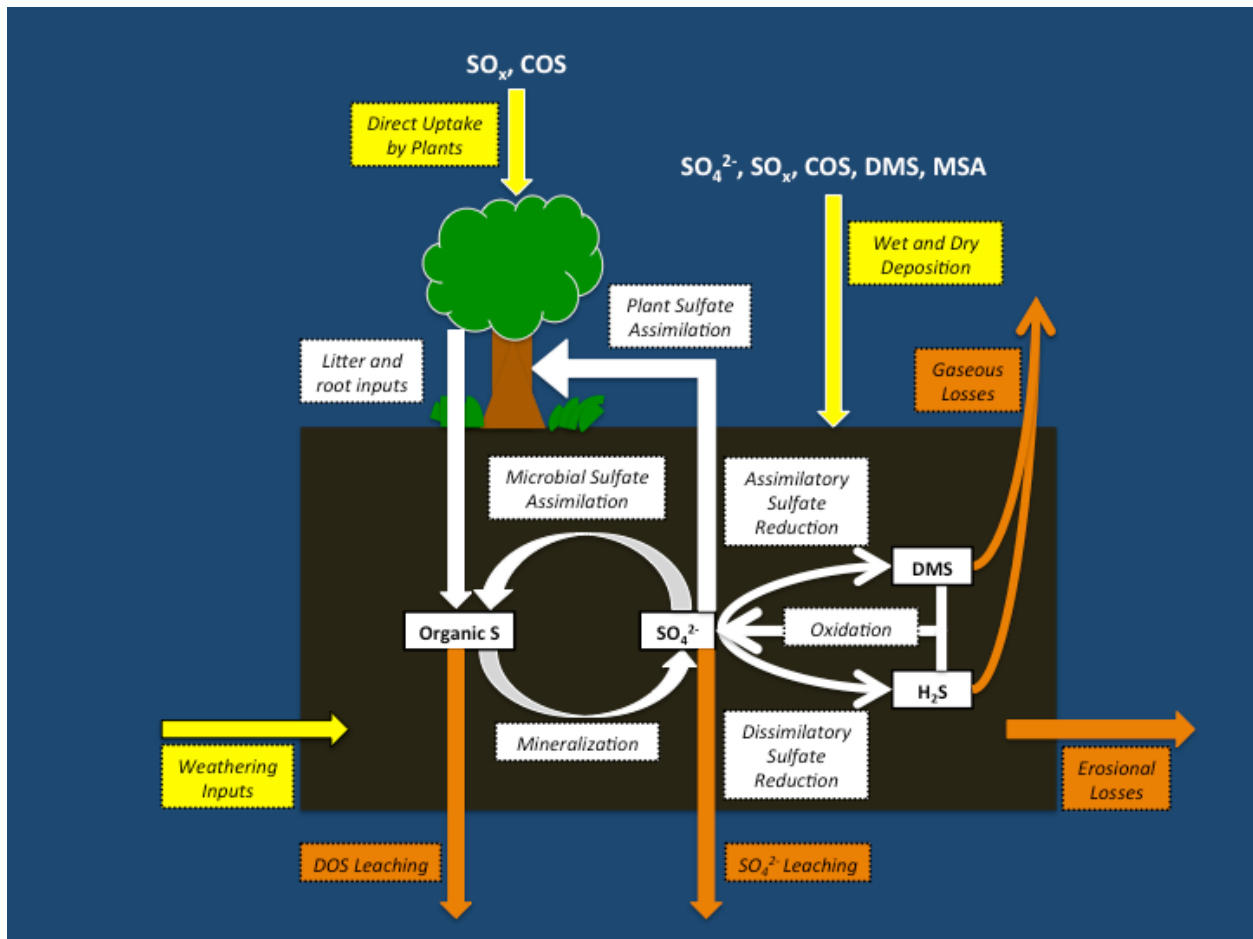
**Figure 2.1:** Organic and inorganic sulphur fractions in soils.

Where S - containing organic compounds: C = Organic S that is not directly bonded to C and is reduced to  $\text{H}_2\text{S}$  by hydriodic acid (HI); D = Organic S that is directly bonded to C (C-S) and is reduced to inorganic sulfide by Raney Ni; E = Organic S that is not reduced by either of the reagents (Tabatabai, 2005a).

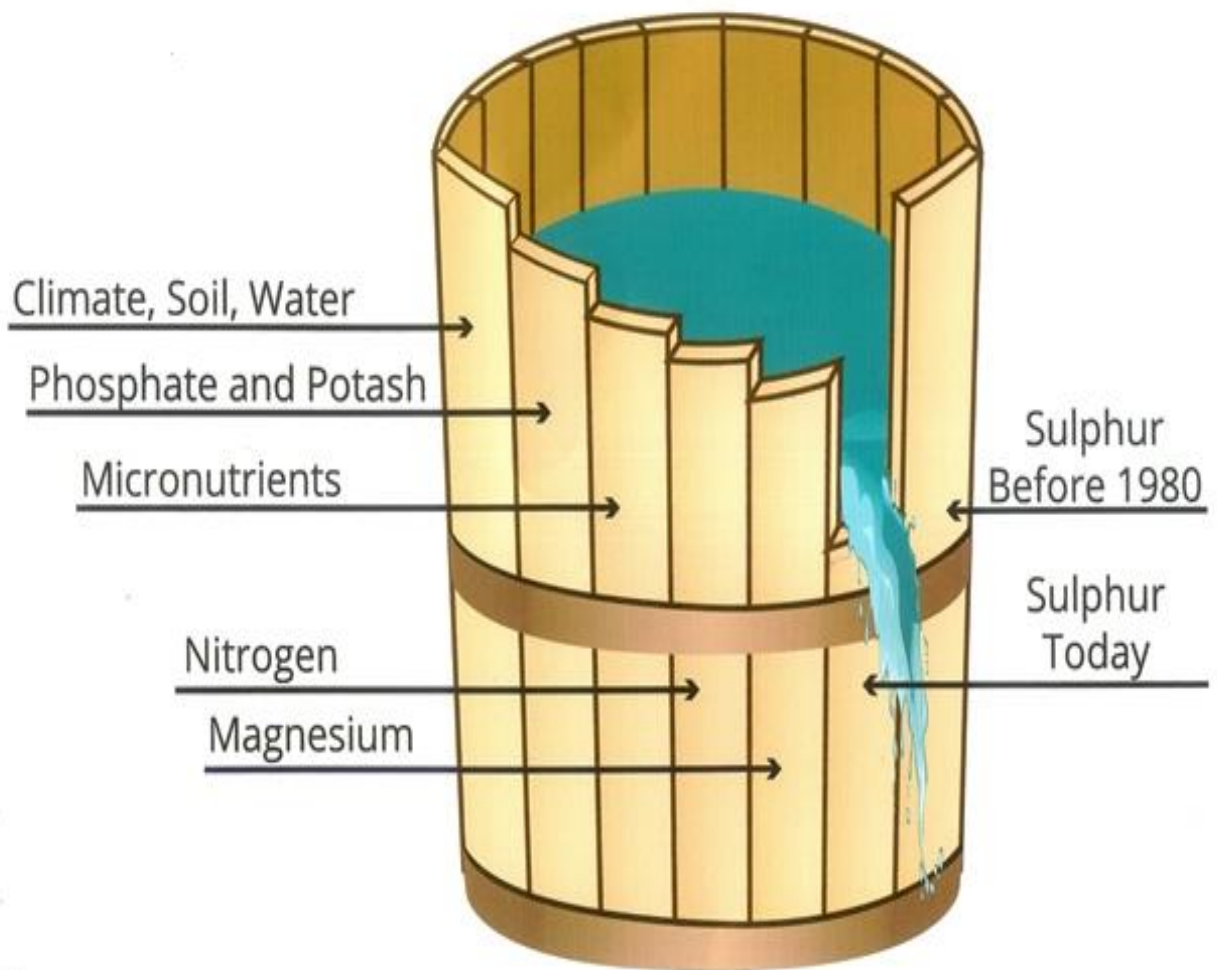
2009). The main reasons for this trend are (1) reduced anthropogenic emission and fossil fuel burning (Likens *et al.*, 2002; Boye *et al.*, 2010), (2) much reliance on high-analysis S-free NPK fertilizers (Boye, 2011), (3) increase of cropping of high yielding crop cultivars such as wheat, cereals and rape-seed (Brimblecombe, 2003), (4) areas where parent materials are low in sulphur and (5) decreased use of S - containing pesticides and fungicides (Fageria, 2009). However, in some soils, sulphur deficiency have been discovered when marginal lands were brought into agricultural practice.

In extension, deficiency of sulphur (S) has been reported in some parts of United States, in particular Southeast, Northwest, California and Great plains (Brady and Weil, 2002). Tisdale *et al.* (1986) reported that sulphur deficiency has been observed in crop plants in 22 African countries. These authors also reported that the majority of the reported S deficiencies in the Africans are in areas south of the Sahara on highly weathered soils that receive over 600 mm minimum rainfall per year.

Recently, Yi-Balan (2013) reported that the most predisposed areas to soil S deficiency are those with low rainfall, such as African, Central Asia, Southern Australia and New Zealand, as well as the continental US. Sulphur deficiency is well recognized problem in Argentina (Boem *et al.*, 2007), Canada (Solberg *et al.*, 2007) and New Zealand (Edmeades *et al.*, 2005). In addition, S deficiency has widely been observed in Nigeria (Kang *et al.*, 1981; Buri *et al.*, 2000; Raji, 2008), Ghana (Acquaye and Kang, 1987) and Ethiopia (Solomon *et al.*, 2001) all for savanna soils. Figure 2.3 illustrates the status of soil sulphur in 1980s as an unlimiting element and today as most limiting plant nutrient in soils.



**Figure 2.2:** Schematic representation of the biotic terrestrial S cycle. Yellow arrows and Boxes represent inputs, orange represents outputs, and white represents biologically mediated transformations within the soil-plant system. (COS: carbonyl sulphide; DMS: dimethyl sulphide; DOS: dissolved organic sulphur; MSA: methane sulphonic acid; SO<sub>x</sub>: sulphur oxides). (Yi-Balan, 2013).



**Figure 2.3:** Current status of sulphur today ([www.Sulphurinstitute.org](http://www.Sulphurinstitute.org).)

## 2.4 Kinetics of Sulphate Adsorption and Desorption in Soils

The capacity of a soil to adsorb or desorb  $\text{SO}_4^{2-}$  could be vital for plant growth and development. However, in the past 3 decades, as concerns and interests about soils and water quality have increased, soil and environmental chemists have increasingly realized that reactions in soil environments are time dependent (Sparks, 2005). Thus, to accurately predict the fate, mobility, and bioavailability of environmentally important plant nutrients like sulphur in soils, one must understand the kinetics of its desorption or release from the soil.

Adsorption is one of the most important chemical processes in soils, and has been one of the most studied aspects of soil chemistry (Sparks, 2002, 2005). Adsorption affects the transport of nutrients and contaminants in soils, and defines the amount of nutrients bioavailable to plants and microorganisms (Burau and Zasoski, 2002; Cichota, 2007). Adsorption is a process of the attachment or disappearance of solutes from soil solution with presumption of them being bonded to a solid phase (Burau and Zasoski, 2002). Despite that usage, the term sorption seems to be appropriate (Sparks, 2002).

The release of adsorbed ions is often referred to as desorption. Despite the fact that most studies in soil chemistry have focused on the adsorption of sulphate by soils and soil constituents, but the desorption process of sulphate is also very important not only in enhancing sulphur availability to plants but also in environmental quality (Alves and Lavorenti, 2006). However, desorption phenomena is often arduous to describe compared to adsorption (Selim and Zhu, 2005; Sparks, 2005; Alves and Lavorenti, 2006). An amount of sulphate desorbed described at a given equilibrium  $\text{SO}_4^{2-}$  concentration in solution through desorption was always lower compared to the amount of sulphate adsorbed during adsorption (Maida and Nalivata, 2016). The reaction may be slower and not all the adsorbed solute may be released. In such cases, the

adsorption and desorption isotherms corresponding to the forward and backward reactions would not coincide (Zhang and Selim, 2005; Wadaskar *et al.*, 2006; Cichota, 2007). The difference between amount of adsorption and successive desorption isotherms reflect the extent of irreversibility for a given  $\text{SO}_4^{2-}$  concentration in soil solution (Reddy *et al.*, 2001; Sammi *et al.*, 2001; Ghosh and Dash, 2012; Maida and Nalivata, 2016). This discrepancy between adsorption and desorption pathways is often referred to as hysteresis and may be caused by operational problems, such as failure to attain equilibrium (Zhang and Selim, 2005).

Nevertheless, real hysteresis can occur and seems to depend especially on the type of adsorbent (Scheidegger and Sparks, 1996; Sparks, 2005). Several studies have pointed occurrence of hysteresis on the adsorption-desorption processes by soils and soil constituents (Strawn and Sparks, 2000; Boivin *et al.*, 2005; Zhang and Selim, 2005; Maida and Nalivata, 2016), however, no real mechanistic information on hysteretic adsorption-desorption of ions has yet been recorded (Burau and Zasoski, 2002; Selim and Zhu, 2005). Moreover, understanding the nature of adsorption mechanisms of sulphate is important, because these mechanisms govern the release of adsorbed sulphate which in turn is assimilated by plants.

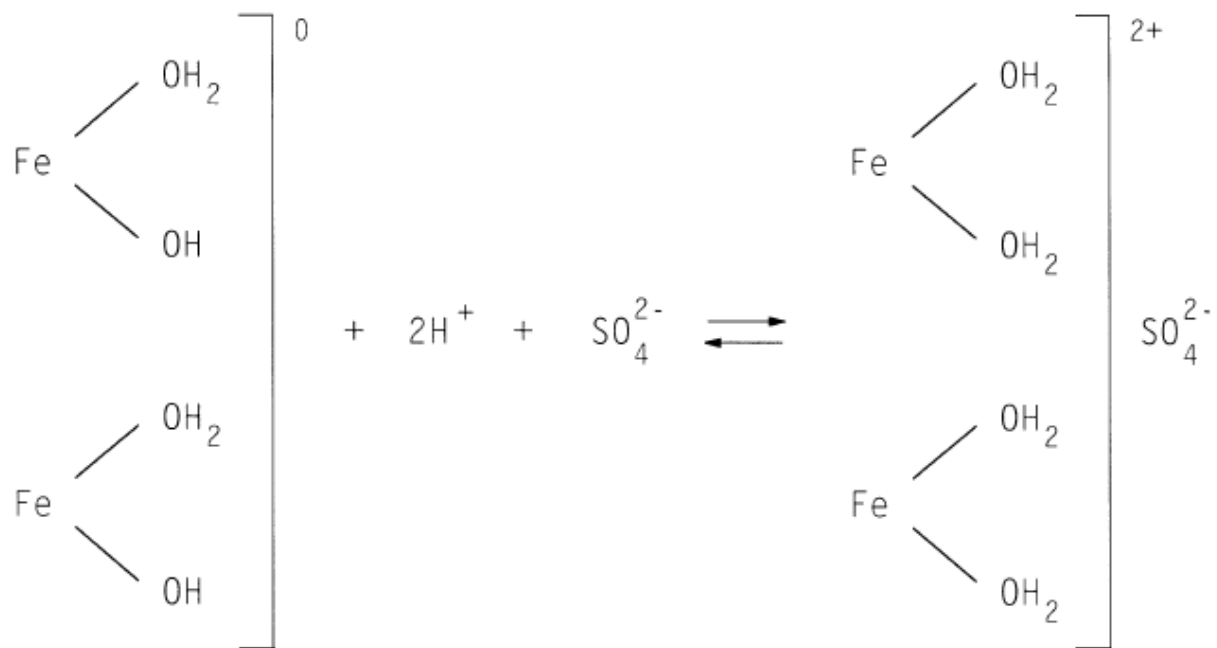
#### **2.4.1 Mechanisms of sulphate adsorption**

In general, anion adsorption is often classified into 2 mechanisms: non-specific and specific adsorption (also called chemisorption or ligand exchange). In nonspecific adsorption, the adsorbate is generally thought to be hydrated and retained by electrostatic forces in the outer Helmholtz plane (Hingston, 1981). Nonspecific adsorption is maintained by electrostatics, as intervening water molecules prevent electron sharing (Essington, 2003). The adsorption process is dominated by the charge that exists at or near the adsorbing surface. In this case, adsorption is

not truly a surface interaction but is an ionic re-arrangement to maintain the electrical neutrality of the system (Ajwa, 1993). Figure 2.4 illustrates the exchange reactions of nonspecific adsorption of  $\text{SO}_4^{2-}$  where positive charges are created due to surface protonation of  $\text{H}^+$  (Bohn *et al.*, 2001).

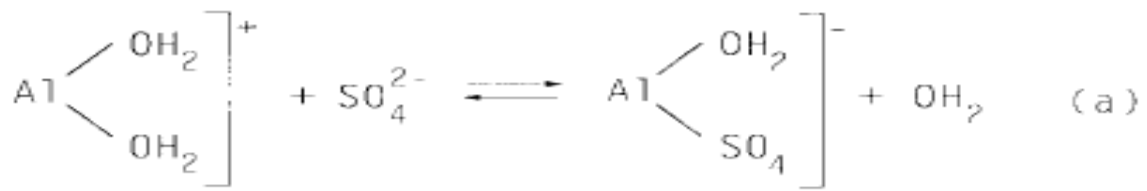
In specific adsorption, the anion is bound by covalent or Van der Waals forces in the inner Helmholtz plane (Hingston, 1981). The term specific adsorption is used for all adsorption that cannot be entirely attributed to electrostatic forces and is formed when sulphate bridges across two Fe or Al atoms to yield a six-membered ring following the displacement of two ligands (OH- and  $\text{H}_2\text{O}$ ) (Rajan, 1978). In specific adsorption, the surface charge plays a less important role in determining which ion is to be adsorbed than in the case of nonspecific adsorption (Ajwa, 1993; Bohn *et al.*, 2001). However, non-specific adsorption mechanism is said to be outer-sphere complexes in contrast, specific adsorption is said to be inner-sphere complexation (Bureau and Zasoski, 2002; Essington, 2003). Rajan (1978) summarized the possible exchange reaction during specific adsorption of  $\text{SO}_4^{2-}$  as illustrated below in Figure 2.5.

Many authors have suggested that mechanisms of sulphate and phosphate adsorption are similar and that both ions compete for the same sorption sites, even though, adsorbed sulphate does not compete strongly with phosphate. Some studies postulated that sulphate may be adsorbed mainly by an outer-sphere complexation mechanism (Bohn *et al.*, 2001; Peak *et al.*, 2001; Ghosh and Dash, 2012; Maida and Nalivata, 2016), in spite of the formation of inner-sphere complexation by sulphate, which may be possible under certain conditions (Agbenin, 1997; Pigna and Violante, 2003; Foloni and Rosolem, 2006). However, the exact mechanisms for sulphate adsorption have not yet been identified (Cichota, 2007).

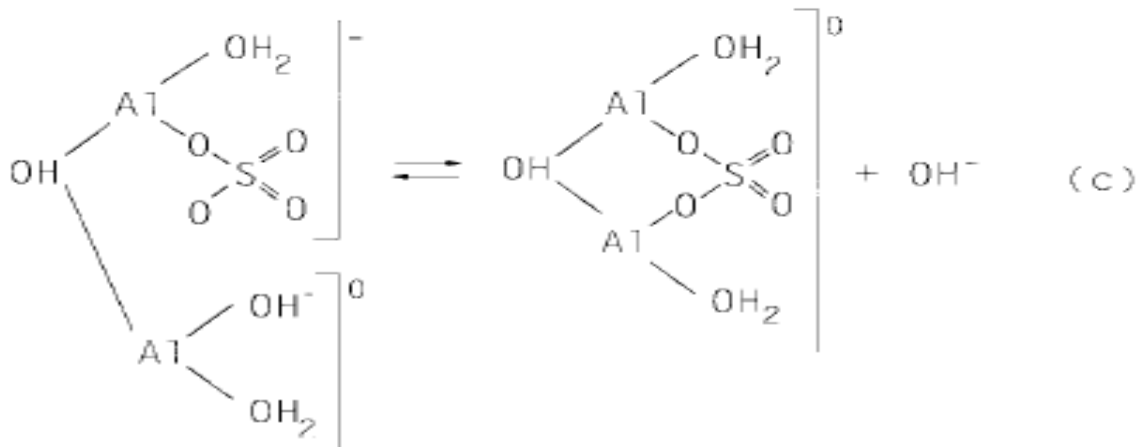
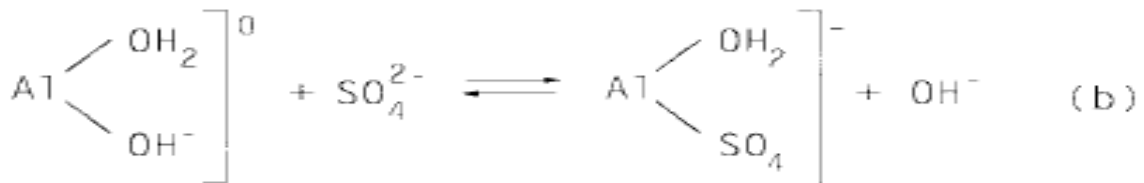


**Figure 2.4.** Protonation of hydroxyl creates formation of net positive charges and results in nonspecific adsorption (Bohn *et al.*, 2001)





or



**Figure 2.5:** Specific adsorption where (a) sulphate displaces water from net positive site, or (b) Sulphate displaces hydroxyl from neutral site and (c) the adsorbed sulphate may displace another hydroxyl or water ligand from the adjoining metal resulting in a 6 - member ring and neutralization (Rajan, 1978).

## **2.5 Factors Affecting Kinetics of Adsorption and Desorption of Sulphate by Soils and Soil Components**

Many factors are responsible for  $\text{SO}_4^{2-}$  adsorption-desorption in soil. These factors are composed of initial  $\text{SO}_4^{2-}$  concentration which is a function of equilibration time, pH, hydrous Fe and Al oxides, type and amount of clay fractions, competing anions, organic matter and cations (metal ions). Each of these factors could be used as an indicator of understanding of mechanism of kinetics of sulphate adsorption and desorption by soils and soil constituents. The following is a discussion of the factors that affect  $\text{SO}_4^{2-}$  adsorption and desorption by soils.

### **2.5.1 Effect of equilibration time**

Equilibrium time is among the significant factors affecting both adsorption and desorption processes by soils. Most reactions in soils are time dependent (Sparks, 2002; 2005; Cichota, 2007). The adsorption of  $\text{SO}_4^{2-}$  can be initially rapid. Rajan (1978) reported that adsorption by hydrous alumina was 90% completed in 10 minutes and 95% complete within 60 minutes with minor change in adsorption after 3 hours. Singh (1984b) reported that 85 and 62% of added  $\text{SO}_4^{2-}$  was adsorbed by an Iron-podzol and Brown earth, respectively, in 24 hours. Marcon-Martinez and McBride (1989) had shown that  $\text{SO}_4^{2-}$  adsorption by soil was almost same after 24 hours and 48 hours. Consequently, most authors considered 24 hours a sufficient equilibration time for  $\text{SO}_4^{2-}$ .

Singh (1984b) compared  $\text{SO}_4^{2-}$  adsorption on two acid forest soils with different incubation time intervals. He revealed that  $\text{SO}_4^{2-}$  adsorption of the Iron podzol soils was completed within 24 hours, but adsorption by brown earth (soils) was only 85%. He also showed that sulphate adsorption in both soils increase over a temperature range of 4 and 24<sup>0</sup>C at a constant initial

$\text{SO}_4^{2-}$  concentration, indicating that  $\text{SO}_4^{2-}$  adsorption is an endothermic reaction. Similar effect of the temperature on  $\text{SO}_4^{2-}$  was obtained by Ajwa and Tabatabai (1995a). Since  $\text{SO}_4^{2-}$  adsorption of soils is relatively rapid, 24 hours of shaking time has been considered by most researchers to be sufficient for complete equilibration (Alves and Lavorenti, 2004; Jung *et al.*, 2011; Ghosh and Dash, 2012; Gustafsson *et al.*, 2015; Maida and Nalivata, 2016).

Sulphate desorption is also time-dependent. Sulphates desorption from soils (Chao *et al.*, 1962b) and kaolinites (Aylmore *et al.*, 1967) have been observed to be rapid. Singh (1984b) reported that desorption of  $\text{SO}_4^{2-}$  was very rapid and completed in half of an hour. Sharpley (1990) found that desorption of  $\text{SO}_4^{2-}$  from soils was rapid and logarithmically related with time to contact between soil and water. He observed that the amounts of sulphate desorbed increased as soil / water ratio increased due to a consequent increase in concentration gradient between adsorbed and solution phases, and decreasing the effect of ionic strength. He also found that approximately 75% of the  $\text{SO}_4^{2-}$  desorbed in 180 minutes was released during the initial 30 minutes of reaction at all soil and water ratios. In similar studies, sulphates desorption from Australian soils (Barrow and Shaw, 1977) and Norwegian forest soils (Singh, 1984b) were almost complete within 30 minutes.

In addition, Rajan (1979) reported complete desorption in 30 minutes. Das and Jena (2009) reported that desorption of the adsorbed  $\text{SO}_4^{2-}$  occurred rapidly for initial 60 minutes during which 73 to 99% of total desorbed  $\text{SO}_4^{2-}$  was released and then slowed down. Almost all the sulphate desorption studies carried out so far explained that maximum desorption (75 to 100%) has been achieved during the initial shaking time of 30 minutes (Garg *et al.*, 2016).

### **2.5.2 Background electrolyte concentration**

The time dependency of sulphate adsorption by soils as affected by the background electrolyte concentration was studied by Courchesne (1991). He showed that, at any time, the amount of sulphate adsorbed by two soil horizons under forest cover in Southern Quebec, Canada, decreased with increasing ionic strength. However, the enhancement of sulphate desorption could be achieved with increasing ionic strength. This could be due to the fact that influence of pH on sulphate sorption was more pronounced at lower electrolyte concentration (Fageria, 2009). Nevertheless,  $\text{SO}_4^{2-}$  adsorption in the absence of supporting electrolyte did not reach a maximum even after 300 hours. Courchesne (1991) also suggested that the amount of  $\text{SO}_4^{2-}$  adsorbed at equilibrium is dependent on the ionic strength of the supporting electrolyte and that the increased of  $\text{SO}_4^{2-}$  adsorption related with decreasing ionic strength is not due to the time dependency of sulphate adsorption.

### **2.5.3 Effect of pH**

Sulphate adsorption and desorption by soils is strongly pH-dependent. The amount of sulphate adsorbed decreases with increasing pH due to a decrease in the electrostatic potential of adsorption plane (Tabatabai, 2005a). As pH decreases and  $\text{H}^+$  becomes more available, more positively charged colloidal surfaces are created which in turn increase the amount of sulphate adsorbed in soils. The adsorption maximum of sulphate has been achieved at pH level around 4.0 (Scherer, 2009). However, if pH is lowered below 4.0, Al and Fe oxides may begin to dissolve and lower the effective positive charge through destruction of the adsorption sites (Ajwa and Tabatabai, 1995a; Lusk, 1998), and desorbility of adsorbed S from adsorption sites can be enhanced.

According to Chao *et al.* (1964) the adsorption maxima of sulphate at pH level around 4.0 occurs only for Al dominated systems and not for Fe dominated soils. This is probably due to the fact that Fe has lower isoelectric point compared to Al, which causes Fe to be more stable at low pH levels. Sumner (1963) working with kaolinite-iron oxide complex found that positive charges decreased with increasing pH until a point is reached in the region 6-7 pH values for goethite or hematite where negative adsorption of anions takes place. Work by Hingston *et al.* (1972) showed that  $\text{SO}_4^{2-}$  adsorption on goethite and gibbsite decreased with increasing soil pH up to 8, beyond which no adsorption occurred.

Maida and Nalivata (2006) studied sulphate sorption and desorption characteristics of selected Malawi soils and observed that soils with pH levels beyond 6 have highest amount of sulphate desorbed value. Numerous researchers have reported negative correlation between sulphate adsorption and soil pH. However, no information is available on effect of pH on sulphate sorption and desorption characteristics in the soils of the Nigerian savanna.

#### **2.5.4 Effect of hydrous Al and Fe oxides and clay minerals**

Increase in the level of hydrous Fe and Al oxides, and kaolinitic clays in acid soils increase sulphate adsorption and reduce sulphate desorption by soils. Some studies showed that high amounts of sulphate are retained in highly weathered tropical soils (Alves and Lavorenti, 2004; Tabatabai, 2005a; Cichota, 2007). This is the fact that hydrous oxides of Fe and Al are ubiquitous in Ultisols, Alfisols, and Oxisols where they often exist as coatings on kaolinitic clays causing these soils to have a high sorption capacity. However, the oxides and hydroxides of Al and Fe possess no permanent surface charge. The positive or negative charge is created by an

adsorption or desorption of  $H^+$  and  $OH^-$  by changing the pH, which result in a surface potential (Ajwa and Tabatabai, 1995a).

Evidence that Fe and Al oxides are related with sulphate retention has been provided by Chao *et al.* (1962b). They removed Fe and Al oxides by chemical treatment, and the resultant soils showed a much lower sulphate adsorption because losses of sulphate via leaching can be enhanced in low retentive soils (soils with no or little amounts of hydrous Fe and Al oxides).

The amount of  $SO_4^{2-}$  adsorbed or desorbed by silicate clay minerals depends on the number of edge adsorption sites. With soil mineralogy in mind, the most important factor is repeatedly the level of Fe and Al oxides present in soils. Harward *et al.* (1962) stated that kaolinite adsorbed more  $SO_4^{2-}$  than montmorillinite. A similar effect of different clay minerals was noted by Chao *et al.* (1962b). They observed that kaolinite adsorbed much more sulfate than bentonite. Cronan *et al.* (1990) compared adsorption between a soils dominated by kaolinitic mineralogy and one dominated by vermiculitic mineralogy and observed significantly higher adsorption by the kaolinitic soil. Clay minerals such as kaolinite can develop significant positive charge under low pH conditions. While pure vermiculite will develop less positive charge than kaolinite. The clay minerals adsorb sulfate in the order: amorphous hydrated oxides > crystalline oxides > kaolinite > illite > bentonite (Mengel *et al.*, 2001). However, the reverse was true for sulphate desorption. Work by Lusk (1998) observed that soils with lower Fe oxide content had little capacity to adsorb additional  $SO_4^{2-}$  and higher sulphate leaching by soils. In general, older, highly weathered soils are thought to have greater adsorptive capacities than younger and less weathered soils. The difference is attributed to a greater development of sesquioxides surfaces in older soils.

### **2.5.5 Effect of organic matter**

Presence of organic ligands in soil solution plays an important role in governing sulphate adsorption and desorption processes in the soils (Tabatabai, 2005a). Although, organic matter may be a source of soluble sulphates by breakdown of ester sulphates (Tabatabai, 2005b), but it may also block sulphate adsorption sites on sesquioxides surfaces. A similar effect of organic matter on sulphate adsorption was noted by Singh (1984b). Organic acids and ligands adsorb to positively charged surface of soils and, therefore, reduces the number of adsorption which in turn enhance sulphate desorption. In addition, sulphate desorption in the soils has been reported to be more comprehensive in soils that are low in Al and Fe oxides, in particular in the A horizons (Parfitt and Smart, 1978).

Ajwa (1993) observed that sulphate desorption and leaching from the A horizon can occur if positive sites of soils are blocked by organic ligands. This is due to the fact that sulphate has a lower binding constant than polycarboxylic acids. Studied by Evans (1991) showed that Dissolve Organic Carbon (DOC) may influence the adsorption/desorption of sulphate in soils either by anion exchange or by preferential adsorption of organic acid on sulphate adsorption sites. Ajwa (1993) also reported that the formation of organic acid-metal bridging complex can be responsible for sulphate desorption and transport in soils.

Comparative studies on the rate of Al release, sulphate desorption, and acid adsorption was done by Evans and Anderson (1990), and Evans (1991). He observed that aliphatic acids may undergo simultaneous chemical reactions involving metal solubilization-chelation, organic-inorganic exchange, and surface desorption. A study by Johnson and Todd (1983) has shown than even when Fe and Al oxides levels are high in soils, the presence of organic matter can still inhibit adsorption, and in turn enhance sulphate availability in S fertilized soils. Moreover, Lusk (1998)

found that shallow surface horizons with high organic matter and low Fe oxide content had higher capacity to desorb sulphate. He also observed that the soils were prone to sulphate leaching. Some studies also showed that sulphate adsorption decrease with increasing organic matter (Mora *et al.*, 2005; Pigna *et al.*, 2007a). This could be attributed either to anion exchange or to preferential adsorption of organic ions on sulphate adsorption sites.

### **2.5.6 Effect of competing anions**

Ajwa and Tabatabai (1995b) reported that the competitive effect of one ion on another is usually expressed in two ways. One is through the physical competition for adsorption sites. The second is through the electrostatic competition resulting from a change in the electrostatic potential in the adsorbing plane following specific adsorption of an anion. However, competition among anionic species in soil solution for the adsorption sites on soil particles can be of major significance in determining the effective mobility of any potentially adsorbing anion species.

Sulphate is adsorbed by soils less strongly than phosphate, and such phenomenon increased the level of desorb sulphate in soil solution. The enhancement of sulphate desorption in presence of phosphate was also reported by Pigna *et al.* (2007a). They noted that soil pH also strongly influences the competition between phosphate and sulphate. Consequently, phosphate solutions are used to extract sulphate in soil tests for S (Fox *et al.*, 1964; Tabatabai, 1982). Increasing the phosphate concentration in solution leads to complete desorption of adsorbed sulphate (Rajan and Fox, 1975). However, Hingston *et al.* (1972) found that sulphate is more strongly adsorption by soils and soil components than nonspecifically sorbed anions, such as chloride.



### 2.5.7 Effect of cations

The presence of other cations in the soil solution is one of the factor governing sulphate adsorption and leaching (Cichota, 2007; Blum *et al.*, 2012). In general the common cations,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}_2^+$ , and  $\text{Mg}_2^+$  are adsorbed by soil minerals when the surfaces are negatively charged (Ajwa and Tabatabai, 1995b), and favour sulphate adsorption (Bolan *et al.*, 1993). This may be attributed to the fact that sulphate can interact with cations, such as calcium, in the adsorption process. Several studies also demonstrated that more sulphate can be expected to be adsorbed when calcium content is elevated (Pigna and Violante, 2003; Mora *et al.*, 2005).

Work by Cichota *et al.* (2007) reported ion adsorption onto particles can be influenced by the presence of other ions in the soil solution. They also noted that same-charge ions compete for adsorption sites, whereas opposite charged ions attract to enhance their adsorption. However, the cooperative interactions between calcium and sulphate may affect their movement through soil solution and also sulphate desorption could be decreased. Several authors (Bolan *et al.*, 1993; Cichota *et al.*, 2007), suggested that specific adsorption of calcium could lead to an increase in positive charge, and enhance sorptivity of sulphate.

In some soils, indeed variable-charge tropical and volcanic soils, increase in sulphate and cation retention, particularly calcium, seems to occur cooperatively. In this process, retention increases in equivalent amounts for both ions (Marcano-Martinez and McBride, 1989; Ajwa and Tabatabai, 1995a). This has been called salt adsorption or ion-pair adsorption (IPA) (Marcano-Martinez and McBride, 1989; Qafoku and Sumner, 2002). So, cooperative retention of opposite-charged ions (IPA) has been identified for the ion-pair sulphate-calcium in some soils with variable-charge characteristics (Marcano-Martinez and McBride, 1989; Bolan *et al.*, 1993). In addition, the adsorption of  $\text{Ca}_2^+$  is believed to create positive charge on oxides (Marcano-

Martinez and McBride, 1989; Cichota *et al.*, 2007), but the magnitude of this charge, detectable as an increase in anion retention, has not yet been reported. Thus, the occurrence of co-adsorption increases the retention of sulphate, and subsequently can retard the sulphate desorption process in soils.

## **2.6 Biochar**

Much of the interest in biochar (BC) comes from studies of Amazonian soils that appear to have been amended with biochar, with significant improvements in soil quality and positive effects on crop yields (Lehmann *et al.*, 2003). Biochar is the carbon rich product produced when biomass such as wood, manure, or plant residues, is heated in a closed container with little or no available atmosphere oxygen. In more technical terms, biochar is produced during a process known as pyrolysis from the thermal-conversion of biomass under limited supply of oxygen at relatively low temperature (<700<sup>0</sup>C) (Lehmann and Joseph, 2009).

Furthermore, pyrolysis temperatures and the type of feedstock strongly influence the capacity of BC to adsorb and desorb nutrients. Singh *et al.* (2010) observed that the soil cation-exchange capacity of manure based biochars is higher than that of wood (Eucalyptus). Slow pyrolysis and lower temperature generally favour BC production, while fast pyrolysis and higher temperatures produce mostly bio-oil with a small amount of biochar (Grantstein *et al.*, 2009). Temperature also affects product quality, and quality affects product value.

Therefore, the incorporation of BC into soil, have been reported to boost soil fertility and improve soil quality by raising pH (Lehmann, 2007; Novak *et al.*, 2009; Cui *et al.*, 2011; Ippolito *et al.*, 2015), increased nutrient sorption efficiency (Laird *et al.*, 2010), soil cation exchange

capacity (Liang *et al.*, 2006; Lehmann, 2007; Sohi *et al.*, 2010), water holding capacity (Herath *et al.*, 2013) and microbial activities (Lehmann *et al.*, 2011; Sohi *et al.*, 2012).

Crop yield improvements with BC have been demonstrated repeatedly for acidic and highly weathered tropical field soils (Lehmann *et al.*, 2003; Rondon *et al.*, 2006). Granatstein *et al.* (2009) observed that the main obstacle for supplementation of BC into soils is that the price for carbon sequestration with BC is not high enough to justify its production. These authors also suggested that direct use of feedstock is more efficient for energy rather than pyrolysis process.

In addition, Lehmann *et al.* (2006) concluded that energy is released more efficiently when biomass (wood) is directly burned to generate energy. They also reported that the process loses the added benefits of supplying or applying BC to soils, such as gains in agricultural productivity, increase in soil pH and payments for C sequestration. In recent studies, Herath *et al.* (2013) reported that a number of logistic and financial constraints limiting the immediate adoption of BC, because of a lack of sound economic evidence for its true agronomic value. Under the current economic situation, growers are unlikely to adopt BC use without greater payback. However, even if growers found BC beneficial they could face difficulty in sourcing quantities large enough for farm application.

Although BC is considered much more effective than the other source of soil amendments, since it is a more stable nutrient source than compost and manure (Lehmann *et al.*, 2009). This may be attributed to longevity of carbon in the soils. However, a detailed review on BC is beyond the scope of this work. Therefore, the literature will be devoted to the effect of BC amendment on sulphate adsorption and desorption in soils.

### **2.6.1 Effect of BC on sulphate adsorption and desorption in soils**

Biochar has a great influence on elements adsorption and desorption in soils due to rise in soil pH. Zhang *et al.* (2016) found that BC supplementation into soil have poor capacity to adsorb and desorb phosphate. Similarly, Novak *et al.* (2009) depicted that BC application in the acidic coastal soils enhance sulphate adsorption which in turn decrease sulphate availability. Recent studies by Cui *et al.* (2011) showed that the P adsorption and adsorption rate on the surface of Fe oxides decreased with the presence of BC, and also enhanced P desorbility of adsorbed P. Several workers suggest that natural OM may increase P solubility through competition with P for sorption sites.

However, studies by Sokolova and Alekseeva (2008) reported that the presence of BC decreased S sorption and the desorbility of adsorbed S can be enhanced. A similar effect of BC has been obtained by Uchimiya *et al.* (2010a) and Borchard *et al.* (2012). In line with interpretation, all emphasized that this increase was probably a consequence of pronounced increase in pH associated with application of BC. In addition to pH, competitive sorption of BC-derived Dissolved organic matter (DOM) can enhance the solubility of S in soils (Kaiser and Zech, 1998; Sokolava and Alekseen, 2008; Borchard *et al.*, 2012). Limited information is available, however, on the effect of BC on sulphate adsorption and desorption in soils, particularly Nigeria savanna soils.

### **2.7 Kinetic models**

The study of desorption kinetics is clearly critically important in predicting the fate of added S and to make proper S fertilizer recommendations in order to enhance crop production in the era of intensive agricultural practice and climate change. In order to examine the mechanisms of

desorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. The study of kinetics of soil chemical process, even in homogeneous systems, is complex and often arduous. When one attempts to study the kinetics of reactions in heterogeneous systems such as soils, and soil components, such as clay minerals, hydrous oxides, and humic substances, the difficulties are greatly magnified (Sparks, 2011). This could be attributed to complexity of soils that are made up of a mixture of inorganic and organic components.

However, kinetic models are designed to provide valuable insights in reaction equilibrium with time and to reveal the mechanism involved in the reaction (Abdu, 2006). In addition, a number of studies have employed different models to compare the goodness of fit of the models for describing S desorption in the soils (Brajendra *et al.*, 2013; Garg *et al.*, 2016). The most used models are the First order, Second order, Elovich, Fractional power and parabolic diffusion models. These models can be transformed into linear forms to obtain adjustable parameters by linear regression analysis.

**2.7.1 First - order equation**

The Lagergren`s first order kinetic model often describe reactions at the soil mineral/water reactions (Sparks, 2002). The first order equation has been successfully used to describe S kinetics experimental data by many authors (Brajendra *et al.*, 2013; Farahmand *et al.*, 2015 Garg *et al.*, 2016).

The first order equation is generally expressed as follows:

$$dq_t/dt = k_1 (q_e - q_t) \dots\dots\dots 2.7.1$$

After integration and applying conditions, for  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$ , the integrated form of equation (1) becomes:

$$\ln q_t = \ln (q_e) - (k_1/2.303) t \quad \dots\dots\dots 2.7.2$$

Where  $q_e$  and  $q_t$  are the amounts of sulphate sorbed / desorbed at equilibrium and at time  $t$  (mg /g), respectively, and  $k_1$  is the rate constant of first- order sorption / desorption (1 /min). Values of  $q_e$  and  $k_1$  are calculated from the slope and intercept of plot of  $\ln q_t$  versus  $t$  (equation 2.7.2).

**2.7.2 Second - order equation**

If the rate of sorption/ desorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation after integration is expressed as:

$$1 /q_t = 1 /k_2 q_e^2 + (1 / q_e) t \quad \dots\dots\dots 2.7.3$$

Where  $q_e$  and  $q_t$  are the amounts of sulphate sorbed / desorbed (mg/g) at equilibrium and at time  $t$ , respectively, and  $k_2$  is the equilibrium rate constant of second order adsorption/desorption (g/mg/min). Values of  $k_2$  and  $q_e$  are calculated from the slope and intercept of the plot of  $1/q_t$  versus  $t$ .

The second order has failed to describe S kinetics desorption data in soils (Brajendra et al., 2013), and also similar results were obtained by Abdu (2006) for P kinetics desorption data, since most of the soils for both studies had shown unappreciable  $R^2$  values and high SE values..

### 2.7.3 Elovich model

The Elovich equation was originally developed to describe the kinetics of heterogeneous chemisorption of gases on solid surface (Sparks, 2005). It seems to describe a number of reaction mechanisms including bulk and surface diffusion and activation and deactivation of catalytic surfaces (Sparks, 2011).

In soil chemistry, the Elovich equation has been used to describe the kinetics of adsorption and desorption of various inorganic materials on soils (Sparks, 2002). The linear form of the Elovich model is presented by the following equation:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \dots\dots\dots 2.7.4$$

Where  $q$  is the amount of sulphate adsorbed/desorbed at a time  $t$ ,  $\alpha$  and  $\beta$  are constants. Thus the constant can be obtained from the slope ( $1/\beta$ ) and intercept ( $(1/\beta) \ln(\alpha\beta)$ ) of the linear plot of  $q_t$  versus  $\ln t$ .

The Elovich equation has been successfully used to describe the kinetics of S desorption in soils (Garg *et al.*, 2016) but has limited utility for describing S adsorption in soils (Farahmand *et al.*, 2015).

### 2.7.4 Fractional power model

The fractional power functional model is a modified form of the Freundlich equation and may be expressed by equation (2.7.5) or its linear form as given in equation (2.7.6) (Ho and McKay, 2002; Sparks, 2011).

$$q_t = kt^n \dots\dots\dots 2.7.5$$

$$\ln q_t = \ln k + n \ln t \quad \dots\dots\dots 2.7.6$$

Where  $q_t$  is the amount of sulphate desorbed at a time  $t$ , where  $k$  and  $n$  are constant with  $n < 1$ . The function  $kn$  is also a constant, being the specific desorption rate at unit time, i.e. when  $t = 1$ . Values of  $k$  and  $n$  are estimated from the slope and intercept of the plot of  $\ln q_t$  against  $\ln t$ . Even though this equation is empirical and the various modified forms have been used by a number of researchers to describe the kinetics of reactions in natural materials (Kou and Loste, 1974; Havlin and Westfall, 1985).

**2.7.5 Parabolic diffusion model**

The parabolic diffusion model is often used to suggest that diffusion – controlled phenomena are rate limiting (Sparks, 2011). This model has been utilized by many authors in describing the kinetics of ion adsorption and desorption in soils (Agbenin and Raji, 2001; Sparks, 2005). The parabolic diffusion equation described P kinetics release on the soils collected from different parent material extremely well which conformed to findings of Abdu (2006).

The equation was also found to describe adequately kinetics of S desorption in soils (Brajendra *et al.*, 2013). The equation can be expressed in the linear forms given by Sparks (2002) as:

$$q_t = R t^{1/2} + b \quad \dots\dots\dots 2.5.7$$

Where  $q_t$  = quantity of S desorbed at time  $t$ ;  $R$  = an overall diffusion coefficient. Thus, a plot of  $q_t$  versus  $t^{1/2}$  and  $b$  is a constant.



The findings that slower reactions at the soil mineral / liquid interface can be described by diffusional models indicates that the kinetics of chemical processes cannot be considered separately from physically limited transport phenomena (Sparks, 2002, 2011). Therefore, such combination processes cannot be treated using first – or other mechanistic kinetic equations. However, there are sites that cannot be reached directly from the liquid phase, but can be reached after sorbate has undergone sorption and desorption at other sites, one can find it difficult to separate chemical kinetics from diffusion-limited kinetics (Sparks, 2002). Abdu (2006) reported that determination of rate-limiting steps is another very important aspect of kinetics study while Agbenin and Rajj (2001) and Abdu *et al.* (2008) used this model to conclude that intra-particle diffusion appeared to be the rate-limiting step in phosphorus release kinetics.

## **2.8 Desorption isotherm equations**

Natural systems are inherently complex, prone to be unstable, and often in dynamic non-equilibrium (Cichota, 2007). To represent such systems, or the processes that are part of it, researchers have been making use of isotherm equations (Sparks, 2002). Thus, numerous computational isotherm models for describing and predicting the dynamics of natural systems have been developed over the past 3 decades (Cichota, 2007; Chen, 2015).

However, this development has been based on the increasing capacity, as well as improved scientific knowledge. The focus of these isotherm models has been for both scientific and practical purposes. The modeling of agricultural systems has brought significant improvements to farm productivity and also has raised awareness to environment concerns (Van den Berg and Driessen, 2002; McCray *et al.*, 2005). The use of model isotherms to predict the fate of added S and to make proper recommendations of S fertilizer is needed nowadays. Isotherms are also used

for suivelling the environmental implications of nutrients additions to agricultural soils (Ledgard *et al.*, 2001; Dragten and Thorrold, 2005).

Simpler isotherm models are also commonly used, as they are easier to handle and can lead to reasonable description of real data. Several mathematical isotherm models have been used to describe ion adsorption and desorption processes. Langmuir and Freundlich are the most common isotherm equations. Consequently, these isotherm models often describe experimental data quite well and can be useful in making comparisons about sorption behaviours between soils even though they provide no mechanistic information (Sparks, 2000). These models have been used to obtain information on binding sites and strength and types of sorption mechanisms (Sparks, 2000, 2005; Ghosh and Dash, 2013; Uzoho *et al.*, 2014). Thus, linear analysis of isotherm data into isotherm equations is an alternative mathematical approach to predict the overall adsorption and desorption processes in soils and soil components. In the past decades, researchers found that it is easier to estimate the parameters by the linear analysis (Chen, 2015), due to their simplicity and convenience. The simple form of the Langmuir and Freundlich models can be described as follows:

**The Langmuir isotherm** (Langmuir, 1916): It is a semi-empirical isotherm model and described by the equation:

$$q_e = q_m k_L C_e / 1 + k_L C_e \dots\dots\dots 2.8.1$$

This equation may be written in several linear forms. One of the most commonly used forms is as follows:

$$C_e/q_e = 1/q_{\max}C + 1/k_L q_{\max} \dots\dots\dots 2.8.2$$

Under ideal conditions, a plot of  $C_e/q_e$  versus  $C_e$  should give a straight line with slope equal to  $1/q_{\max}$  from which  $q_{\max}$  is estimated. The  $k_L$  is constant calculated from the intercept (Ajwa and Tabatabai, 1997; Farahmand *et al.*, 2015). Another linear form of the isotherm is a plot of  $1/q_e$  against  $1/C_e$  (Farouq and Yousef, 2015). Such a plot is less reliable in estimating the Langmuir parameters despite a marked improvement in the correlation coefficient values (Ajwa and Tabatabai, 1997). Therefore, a high coefficient of determination does not ensure a best fit of the isotherm model to ion adsorption by soils and other materials (Harter, 1984; Kuo, 1988). Thus, a plot of  $C_e/q_e$  against  $C_e$  is usually superior to the plot stated above, and  $q_e$  versus  $q_e/C_e$  plot (Kuo, 1988; Ajwa, 1993).

This isotherm model is based on 3 assumptions, namely adsorption limited to monolayer coverage, all surface sites being alike, and one site accommodating one adsorbed atom and the ability of a molecule given independent of its neighbouring sites occupancy. The Langmuir isotherm model has been successfully used to describe S adsorption and desorption in soils (Ajwa and Tabatabai, 1997; Lusk, 1999; Osodeke and Ubah, 2006; Farahmand *et al.*, 2015; Maida and Nalivata, 2016).

**Freundlich isotherm model** (Freundlich, 1906): It is a purely empirical isotherm model and based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially to the heat of adsorption. The Freundlich isotherm model is one among the most widely used isotherm for

description of kinetics adsorption and desorption of equilibrium data. The adsorption isotherm is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \dots\dots\dots 2.8.3$$

This can be linearized as:

$$\ln q_e = \ln k_f + 1/n_f \ln C_e \dots\dots\dots 2.8.4$$

Where,  $q_e$  is the amount of sulphate desorbed at equilibrium (mg/g) at any time (t), and  $C_e$  is the concentration of sulphate ion in solution (mg/L).  $K_F$  (L/g) and  $1/n_F$  are the Freundlich constants related to desorption capacity and desorption intensity, respectively.

The Freundlich constants  $K_F$  and  $1/n_F$  are calculated from the slope and intercept of the  $\log q_e$  versus  $\log C_e$  plot. As a robust equation, Freundlich isotherm model has the potentiality to fit almost into all experimental data, and in particular best for highly heterogeneous sorbent systems (Alves and Lavorenti, 2004; Jung *et al.*, 2011).

Three major problems arise when using the simple form of adsorption or desorption isotherms for modeling the fate of ions in the soils. Firstly, these equations imply that the reactions in the soils are rapid, so that the soil solution system remains always in equilibrium. However, the dynamics of sorption (adsorption and desorption) processes should not be neglected for an accurate prediction of the fate and movement of solutes in the soils (Zhang and Selim, 2005; Wadaskar *et al.*, 2006; Cichota, 2007) contrary to the statement mentioned above. Of course this depends on the level of detail and degree of confidence desired and characteristics of the system being described (Sarkar *et al.*, 2006).

A division of the process into instantaneous and time dependent reactions may also be employed (Selim *et al.*, 2004). The second problem involved in the use of simple isotherm equations is that variations in soil temperature and pH or salt concentration can be significant. This may result to uncertainties to levels beyond acceptability (Cichota, 2007). To elude discrepancies, one must use isotherms under similar conditions to those in which they have been determined. Also, by using sub-functions of the isotherms parameters based on soil pH or temperature such problems will be solved (Sullivan *et al.*, 2003). The third issue to be considered when using simple adsorption or desorption isotherm models is whether the adsorption and desorption processes follow the same relationship. Discrepancy interactions with the environment, and in particular different dynamics, can alter the equilibrium between adsorbed and solution phases, resulting in hysteresis (Cichota, 2007). This has been observed in numerous studies (Selim and Zhu, 2005; Wadaskar *et al.*, 2006; Ghosh and Dash, 2012; Maida and Navilata, 2016), although the effects were small or non-existent in other previous studies (Aylmore *et al.*, 1967).

Despite these problems, it seems that the Langmuir and Freundlich equations are still valuable in the modeling of solute adsorption. This was probably due to their simplicity and small number of parameters, the data set needed for a reasonable description using these equations can be relatively small (Cichota, 2007). Also in many cases, the predictions using such simple models can be comparable in accuracy with predictions from more complex models (Wu *et al.*, 2002; Dubus *et al.*, 2004). Being simple, they can be easy to handle and can be incorporated into larger environmental isotherm data (Cichota, 2007).

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Site Descriptions

The study was conducted in 2017 in Bauchi North of Bauchi State (Figure 1 and 2), and geographically falls within Nigerian Sudan savanna. Soils in the state are formed from Basement Complex rock (BCR) and the Sedimentary Rocks comprising the Kerri-Kerri formation (KKF) and the Chad formations (CF). The CF covers most part of the Bauchi north, and BRC of the state (Mustapha, 2003). For details see description in Table 3.1.

The vegetation is an open savanna wood land with trees up to 6m or more. The trees normally occurs singly or in clusters, while spaces within are occupied by non-woody species up to 3m high. Grasses in the area reach up to 2m and above. The natural vegetation consists of *Hyparrhenia*, *Ripania spp* and *Andropogon* as grasses and scattered *Tamarindus indica*, *Pankia clapertania* and *Khaya senegallensis* as the dominant trees. Some of the crops grown in the area include rice (*Oryza sativa*), tomato (*Lycopersicon lycopersicum*), and maize (*Zea mays L*) and pepper (*Capsicum annum*).

The climate of the study area is typically tropical with distinct rainy and dry seasons. The rainy season starts on the average in June-July and ends in November. The dry season lasts from November-May. The rainy season is characterized by high temperature and special variation, averaging about 280 mm per annum. The amount of rain falls annually is 616 mm per annum in the Bauchi North (Murabbi, 2012). Temperature ranges from 16 to 35°C. Nights are cool (12°C) from November through February. March and April are very hot with night temperature ranging from (25 to 30°C) and day time as high as 38 to 42°C (Hassan *et al.*, 2016).

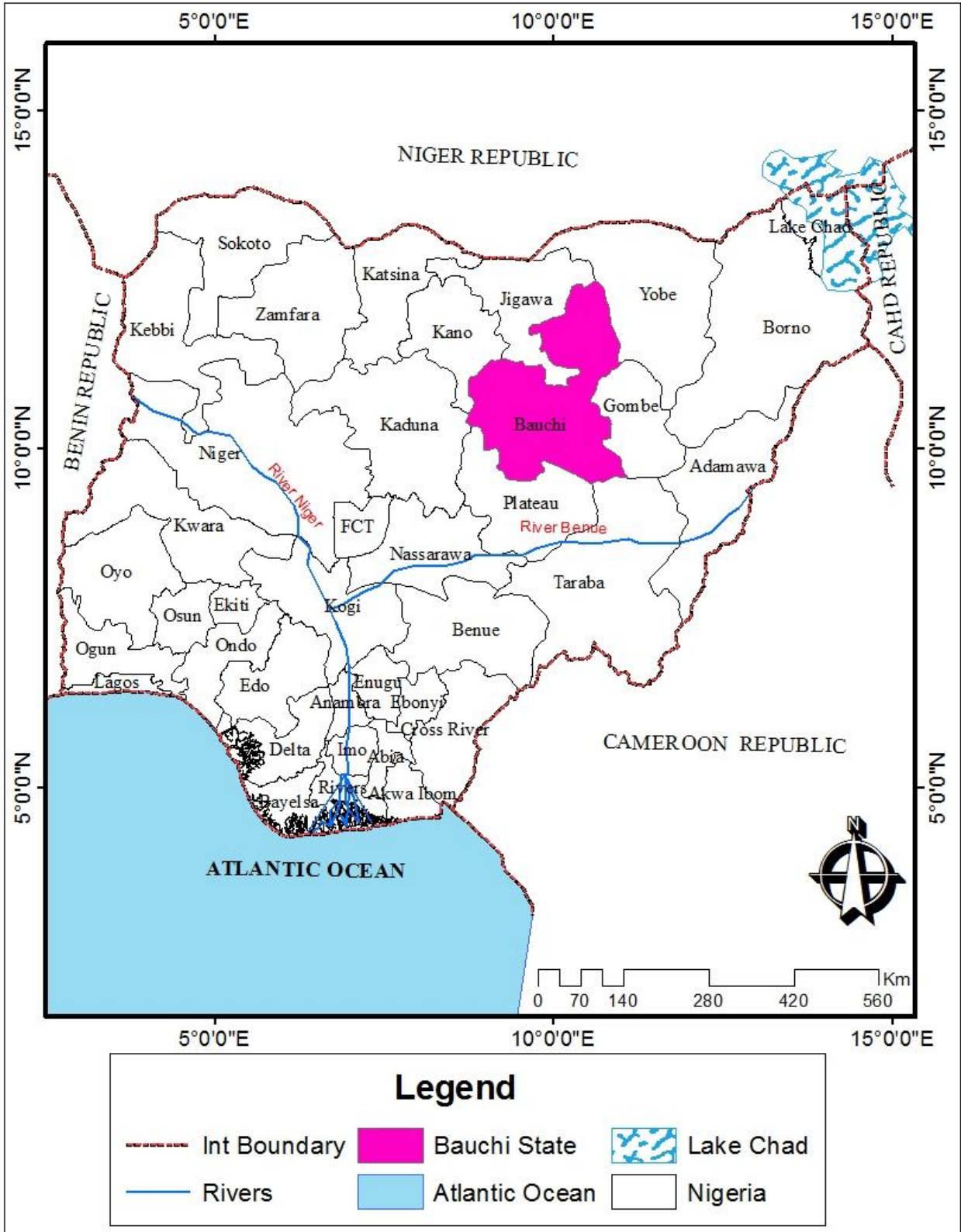
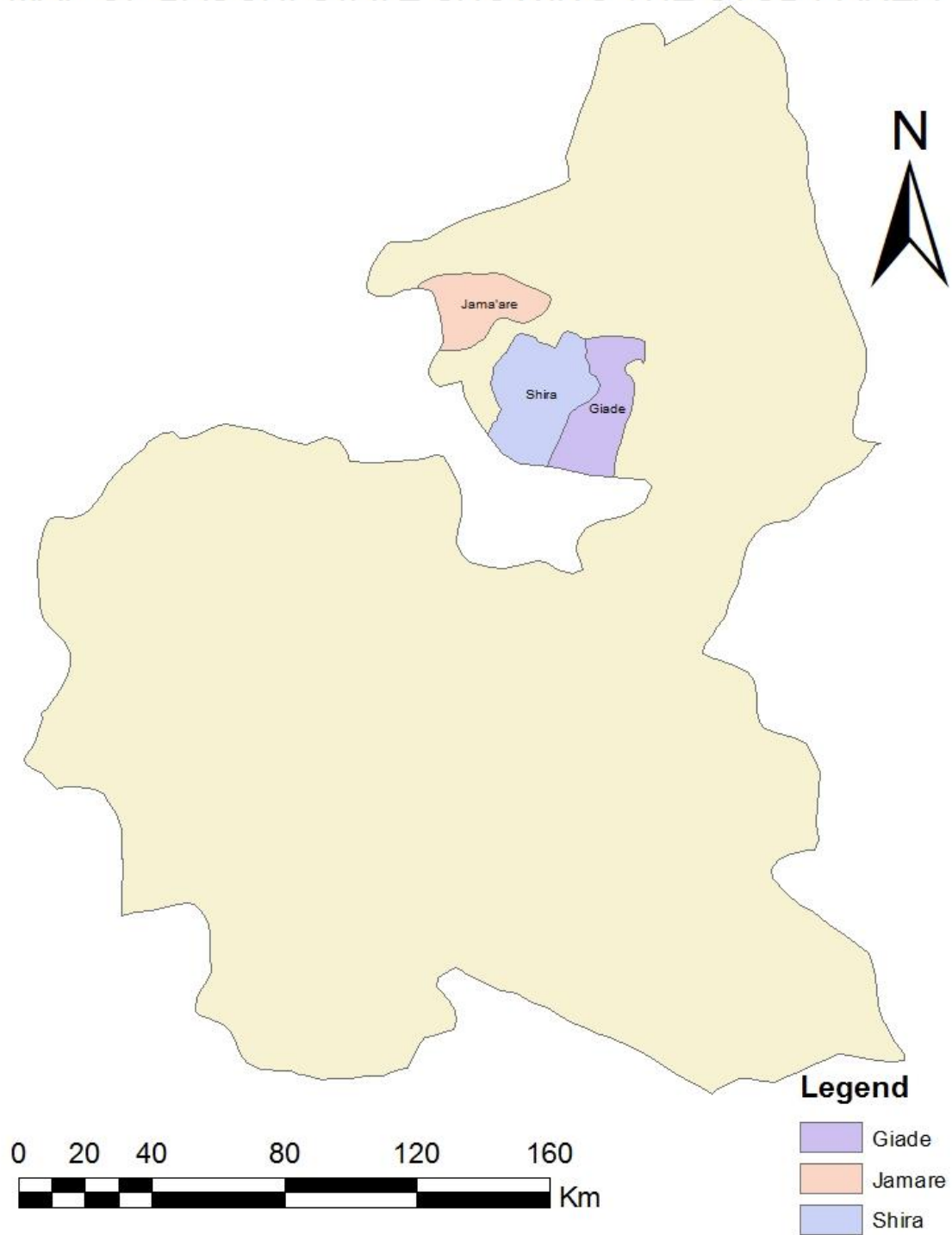


Figure 3.1. Map of Nigeria showing Bauchi state

# MAP OF BAUCHI STATE SHOWING THE STUDY AREA



**Figure 3.2.** Map of Bauchi state showing study sites



### **3.1.1 Soil Sampling**

Soil samples were collected from 3 different parent materials (Chad Formation (CF), Basement complex rock (BCR) and Kerri-Kerri Formation (KKF)). Three uncultivated sites were selected after a reconnaissance survey from each soil parent material to eliminate effects of external factors such as fertilizer applications (Table 3.1). At each location, twenty (20) auger soil samples were randomly collected at 0-15cm (surface) and 15-30cm (sub-soils) soil depths and replicated twice. One composite soil sample at each depth was prepared from the 20 auger soil samples collected making of four (4) composite samples per location. The same pattern was applied to the rest of the locations for the different parent materials. Thus, making a total of 36 (2×2×3×3) composite soil samples. The samples were taken in polyethenes bags to the laboratory for Analysis.

### **3.1.2 Sample preparation**

The soils were air-dried on clean polythene bags in a well-ventilated environment for one week. After drying, samples were ground with porcelain pestle and mortar and sieved to remove materials greater than 2 mm fraction. The sieved soil samples were used for all laboratory analyses.

**Table 3.1 GPS location, geology, and selected physiographic features of the study sites**

Location	Coordinates	Altitude (m)	Geological formation	Ecology	Dominant soil group
JAMA'ARE Digiza	11° 39 <sup>1</sup> N 9° 57 <sup>1</sup>	380.50	Chad Formation	Shrubs	Alfisols
JAMA'ARE Gongo	11° 41 <sup>1</sup> N 9° 56 <sup>1</sup>	386.00	Chad Formation	Short grasses & deciduous trees	Alfisols
JAMA'ARE Guda	11° 38 <sup>1</sup> N 9° 55 <sup>1</sup>	387.60	Chad formation	Neem Forest	Alfisols
YANA Tawayla	11° 24 <sup>1</sup> N 9° 59 <sup>1</sup>	407.90	Basement complex rock	Shrubs	Alfisols
YANA Jaberi	11° 23 <sup>1</sup> N 10° 0 <sup>1</sup>	416.50	Basement complex rock	Shrubs	Alfisols
YANA Zenabari	11° 23 <sup>1</sup> N 10° 3 <sup>1</sup>	428.50	Basement complex rock	Neem Forest	Alfisols
GIADE Kauyan-Jalo	11° 23 <sup>1</sup> N 10° 12 <sup>1</sup>	467.70	Kerri-Kerri formation	Shrubs	Alfisols
GIADE Doguwa	11° 23 <sup>1</sup> N 10° 10 <sup>1</sup>	461.80	Kerri-Kerri formation	Shrubs	Alfisols
GIADE Kwari	11° 24 <sup>1</sup> N 10° 11 <sup>1</sup>	423.50	Kerri-Kerri Formation	Mango Forest	Alfisols

**Location with full capital is name of Local Government**

## 3.2 Characterization of the soils

### 3.2.1 Particle size distribution

Particle size distribution was determined by Bouyoucos hydrometer method after dispersion with sodium hexametaphosphate (Gee and Bauder, 1986). Fifty gram of 2 mm sieved soil was placed into polythene bottle and 25 ml of Calgon solution and 400 ml of water were added and shaken for 15 min on mechanical shaker. The soil suspension was transferred to a 1 litre capacity cylinder and made to mark with water. The suspension was thoroughly stirred using a plunger and a hydrometer. The readings were recorded at 40 seconds and after 2 hours. A blank of the reagent was run and percentage of clay, silt and sand to be determined as follows:

$$\text{i. } \% \text{ Clay} = \frac{\text{Correction 2 hours hydrometer reading} \times 100}{\text{Weight of soil taken}}$$

$$\text{ii. } \% \text{ Silt} = \frac{\text{Corrected 40 seconds hydrometer reading} \times 100}{\text{Weight of soil taken}}$$

$$\text{iii. } \% \text{ Sand} = 100 - (\% \text{ Silt} + \% \text{ Clay})$$

$$\text{iv. } \text{Corrected reading } C = (\text{Actual reading} - \text{Blank reading}) + 0.36T$$

Where  $T$  is the room temperature minus  $20^{\circ}\text{C}$ .

The textural class was obtained using the international soil textural triangle.

### 3.2.2 Soil pH

Soil pH was determined using 1:1 soil/water and 1:1 soil/0.01M  $\text{CaCl}_2$  using glass electrode meter as follows: Ten gram of 2 mm sieved soil was placed into a 36 plastic cups and 25 ml of

distilled water was added gradually until the soil was wetted. The suspension was then stirred thoroughly with a glass rod and the pH was measured by inserting the glass electrode meter into the soil suspension. The same procedure was applied but using 0.01M CaCl<sub>2</sub> solution instead of water but suspension was allowed to stand for 30 minutes with occasional stirring after the addition of CaCl<sub>2</sub> solution.

### **3.2.3 Organic carbon**

Organic carbon (OC) was determined by Walkley – Black dichromate wet oxidation method (Nelson and Sommers, 1982). One gram of 2 mm sieved soil sample was weighed into a 250 ml conical flask. Ten milliliters of 0.1N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution were added and the flask was swirled gently to disperse the soil. This was followed by the addition of 20 ml of H<sub>2</sub>SO<sub>4</sub> concentration and thoroughly mixed. The mixture was left for half of an hour and allowed to cool down. Twenty milliliters of distilled water were added and the whole suspension was filtered through What man No.1 filter paper. Three drops of Ferroin indicator were added and titrated with 0.4N ferrous ammonium sulphate solution. The end point was reached when the colour changed from dark green to red. Blank determination was made in the same manner. Organic carbon in the soil was calculated as:

$$\text{OC} = \text{Meq of Cr}_2\text{O}_7 - \text{Meq of Fe-NH}_4\text{SO}_4 \times 3 / \text{weight of soil sample}$$

### **3.2.4 Exchangeable cations and cation exchange capacity (CEC)**

Exchangeable cations were extracted with neutral 1 N ammonium acetate with potassium (K) and sodium (Na) determined by flame photometry and calcium (Ca) and magnesium (Mg) by EDTA titrations. Ten grams of 2 mm sieved soil samples was weighed into 50 ml centrifuge

tubes, 33 ml of 1N NH<sub>4</sub>OAc solution was added stirred and left over night. The suspension was leached with 1N NH<sub>4</sub>OAc solution to a volume of 250 ml. The soil was leached again with 1N NH<sub>4</sub>Cl solution four times and the solution was discarded. The soil was leached with acidified 0.1 N NaCl solutions and the leachate was transferred into Kjeldhal flask and distilled over 2% boric acid solution in a conical flask. One hundred and fifty milliliters of the leachate was collected and titrated with 0.1N HCl solution. Cation exchange capacity was computed from the relation:

$$\text{CEC} = [(\text{Titre-B}) \times \text{NA} \times 100 / \text{weight of soil (g)}]$$

Where B = blank, NA= normality of the acid

### 3.2.5 Base saturation

This was estimated as follows:

$$\text{Base Saturation, BS (\%)} = [\text{Total of Exchangeable Bases (cmol (+) kg}^{-1} \text{ soil)} / \text{CEC (cmol (+) kg}^{-1} \text{ soil)}]$$

### 3.2.6 Total sulphur

Total sulphur in soil was determined according to Tabatabai (1982), by wet oxidation of soil sulphur compounds to sulfate using alkaline sodium hypobromite (NaOBr) solution.

### 3.2.7 Inorganic sulphur

Sulphate in soil was extracted with 500 mg P L<sup>-1</sup> as Ca (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (Fox *et al.*, 1964) and all filtrate extracts were analyzed for sulphate concentration by the turbidimetric method of Tabatabai (1982).

### **3.2.8 Organic sulphur**

Organic S was normally estimated from the difference between total S and inorganic S values determined independently (Tabatabai, 1982; Neptune *et al.*, 1975).

### **3.2.10 Extractable Al and Fe oxides**

Oxalate-extractable Al and Fe were determined by extraction with ammonium oxalate in the dark (Jackson, 1986) as follows: Half gram of soil was placed into 50 ml centrifuge tubes and 25 ml of 0.2 M acidified ammonium oxalate solution buffered at pH 3.0 was added. The tube was shaken mechanically in the dark for 4 hours. The suspension was centrifuged for 30 min and the clear supernatant solution was decanted into clean vials. Ten milliliters of the extract were measured into 100 ml volumetric flask and diluted to mark with distilled water. Iron in the solution was determined by AAS and Al by Aluminon Method.

Dithionite-citrate-bicarbonate-extractable Fe and Al were determined by the method of Mehra and Jackson (1960). One gram of 2 mm sieved soil was placed into a centrifuge tube and 40 ml of 0.3 M sodium citrate solution was added together with 5 ml of 1 M sodium bicarbonate solution. The soil suspension was heated on a water bath at 70-80°C. One gram of sodium dithionite salt was added to the solution and stirred continuously for 1 min and occasionally for 15 min. The suspension was centrifuged and the clear supernatant solution was decanted into a 200 ml flask. The residue was treated with sodium citrate-sodium bicarbonate-sodium dithionite once again. The soil was then washed twice with 40 ml of 0.3 M sodium citrate solution and then centrifuged and decanted. The clear supernatant solution was added to the extract in the 200 ml flask and made to mark. Iron in the solution was determined by AAS and Al by aluminon method as described by Jackson (1958).

### **3.2.8 Sodium pyrophosphate extractable Fe and Al**

Organic forms of Fe and Al were extracted using pyrophosphate solution as described by McKeague (1967). Two grams of 2 mm sieved soil was placed into 500 cm<sup>3</sup> plastic bottle. Two hundred cubic centimeters of 0.1M sodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) were added by means of a pipette. The bottle was closed and shaken overnight in a reciprocating shaker. Twenty five cubic centimeters of the suspension were transferred into a 50 cm<sup>3</sup> and centrifuged for 30 minutes at 4,500 rpm. The extracts were somehow turbid. A high speed centrifuge was needed to clear the pyrophosphate extract because on extraction the soil was highly coloured.

Iron in the extract was determined after ten times dilution by the AAS at 373.9 nm wavelength. The concentration of iron was obtained from a standard curve.

Aluminium in the extract was determined by the Aluminon method as described by Jackson (1958) as follows: Ten cubic centimeters of extract was pipetted into a 50 cm<sup>3</sup> volumetric flask. One cubic centimeters of 0.5 percent ascorbic acid was added and heated for 30 -35 minutes on hot water bath (80-90°C). It was cooled to ambient temperature and 35 cm<sup>3</sup> of water was added. After mixing, 10 cm<sup>3</sup> Aluminon-acetate buffers was added and water was added to mark. The pH was controlled at 3.7 to 4.0 with HCl. The colour intensity was measured after 2 hours on a spectronic 20 at 530 nm wavelength. The concentration of aluminium was obtained from a standard curve.

### **3.2.9 Preparation of stock sulphate solution**

To prepare a stock solution, 1.81 g of K<sub>2</sub>SO<sub>4</sub> was dissolved in small amount of distilled water and then complete to total of volume of 1 litre to give a concentration of 1000 mg/L. To obtain further required concentrations, the stock solution was diluted appropriately.

### 3.3 Kinetic Experiments

#### 3.3.1 Kinetics of desorption of added sulphate

For the sorption experiment, 2.5 g of 2 mm sieved soil was placed into separate plastic tubes and added 15ml of 0.01M of NaCl containing 50 mg S g<sup>-1</sup> (K<sub>2</sub>SO<sub>4</sub>) from a stock sulphate solution of 1000 mg S g<sup>-1</sup>. The soil samples were shaken intermittently for a predetermined equilibrium time of 24 hours. After equilibration, the samples were filtered. The filtrate thus collected was analyzed for SO<sub>4</sub><sup>2-</sup> by turbidimetric method of Tabatabai (1982). Sulphate adsorbed was calculated as the difference between sulphate added and sulphate remaining in solution.

For desorption experiment, soil sample with adsorbed S after separating solution sulphate was used for the desorption study. Soil sample was shaken with 15 ml of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solution containing 500 mg P l<sup>-1</sup> for 30, 60, 150, 180 and 240 minutes. After shaking, the supernatant was filtered and analysed for SO<sub>4</sub><sup>2-</sup> by the turbidimetric method of Tabatabai (1982). The amounts and percentages of sulphate desorbed were calculated with respect to the sorbed SO<sub>4</sub><sup>2-</sup> as follows:

$$\text{SO}_4^{2-} \text{ desorbed (mg/g)} = \text{SO}_4^{2-} \text{ recovered (mg/g)} - \text{analyzed SO}_4^{2-} \text{ in solution (mg/g)}$$

$$\text{SO}_4^{2-} \text{ desorption (\%)} = \frac{\text{Sulphate desorbed (mg/g)}}{\text{Sulphate adsorbed (mg/g)}} \times 100$$

### 3.4 Effect of Biochar on Sulphate Desorption Rate

#### 3.4.1 Biochar preparation and application

Maize stalk for biochar production was collected from Department of Soil Science, Faculty of Agriculture, Bayero University Kano, Kano State. The biochar was produced at 500°C pyrolysis temperature based on the recommendation of Lehmann (2007). After the pyrolysis process, the biochar was ground to small granules and passed through 2 mm sieve in order to have the same particle size as that of the soils.



Potassium sulphate (in 15 ml of 0.01M CaCl<sub>2</sub> solution containing 500 mg S g<sup>-1</sup> as K<sub>2</sub>SO<sub>4</sub>) was added into 2.5 g of soil in plastic tubes. The biochar was applied at rate of 50,000 kg dry biochar / ha (calculated rate of biochar from rate of 50 tones / ha to incorporate with 2.5 g of soil is 0.06g of biochar) and then thoroughly mixed into the sulphur - added soils. The soils were brought to field capacity initially with distilled water. The soil samples mixed with biochar (BC) were also incubated for 7 days. After the analysis, desorption of adsorbed sulphate was done in same pattern described above.

### 3.5 Fitting of Sulphate Desorption Data to Sorption Isotherms

It is integral to evaluate the most appropriate correlation for equilibrium curves to optimize the design of a desorption system. The Langmuir and Freundlich equations were selected to describe the desorption equilibrium of soil without biochar because of their simplicity and ability to fit a wide range of adsorption-desorption data. The data was fitted to both the Langmuir and Freundlich adsorption isotherms. The two isotherms have been described in detail in section 2.8.

### 3.6 Kinetics Modeling of Sulphate Desorption

Kinetic data was fitted to the following equations which have been previously described in detail in section 2.7.

#### First Order Model

$$(\ln q_t = \ln (q_0) - (k_1/2.303) t) \dots\dots\dots 3.6.1$$

#### Second - Order Equation

$$(1 / q_t = 1 / k_2 q_e^2 + (1 / q_e) t) \dots\dots\dots 3.6.2$$

#### Elovich Model

$$(q_t = 1 / \beta \ln (\alpha\beta) + 1/\beta \ln t) \dots\dots\dots 3.6.3$$

### **Fractional Power Model**

$$(\ln q_t = \ln k + n \ln t) \dots\dots\dots 3.6.4$$

### **Parabolic Diffusion model**

$$(qt = R t^{1/2} + b) \dots\dots\dots 3.6.5$$

## **3.8 Statistical Analysis**

Two-way Analysis of variance (ANOVA) was used to analyse the variation among parent materials and between the soils desorption data (with biochar and without biochar). The 3 parent materials, locations, depths, and soils (with biochar and without biochar) were regarded as the treatments whereas; replicate samples and shaking times were considered as the replication or random, respectively. Means that were statistically significant were separated by the Least Significant Difference (LSD). All the statistical analyses were carried out at 95% confidence level using SAS 9.2 (2011).

### **3.8.1 Fitness of the kinetic models and isotherm equations**

Goodness of fit is an essentially important parameter that estimates how well the curve describes the experimental data. The linear forms of the kinetic and isotherm equations were fitted to the experimental data. Least square regression analysis was used to ascertain the model or equation that best described sulphate desorption kinetics in the soil from the study sites. It is assumed that the model or equation which gives the highest  $R^2$  and lowest standard error of estimates (SE) values is the best model or equation for describing sulphate desorption data. The standard error was calculated as follows:

$$SE = \sum [(S_a - S_b)^2 / (n-2)]^{0.5}$$

Where  $S_a$  and,  $S_b$  represent the measured and predicted sulphate desorbed, respectively, and  $n$  is the number of measurement. The relationships between desorption coefficients and soil properties were investigated by correlation analysis using IBM SPSS version 20.0 (2012).

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

#### 4.1 Soil Physical and Chemical Properties

The physical and chemical properties of soils from three parent materials, namely; Chad formation (CF), Basement complex rock (BCR) and Kerri-Kerri formation (KKF) is shown in Table 4.1. Sand content was dominant in all the three soil parent materials (Table 4.2), having higher values in surface soils compared to their corresponding sub-surface soils (Table 4.1). Similar results were obtained by Odunze (2006), Obi and Akinbola (2009), Obalum *et al.* (2012), Maniyunda *et al.* (2014) and Hassan *et al.* (2016) all for different Nigerian savanna soils. However, silt content ranged from 55.60 to 225.60 g/kg with higher value from soils developed over BCR (Table 4.1). Clay content is higher in the subsurface soil than in the top soil (Table 4.1), and is attributable to clay illuviation and eluviation in surface soils (Obi and Akinbola, 2009; Maniyunda *et al.*, 2014 and Hassan *et al.*, 2016). The mean values of sand, silt and clay fractions in soils from the three parent materials did not significantly vary ( $p > 0.05$ ) (Table 4.2). The lack of differences might be attributed to the old nature of tropical soils that are generally highly weathered. Generally, the soils were dominantly sandy loam except in some soils developed from BCR and KKF (Table 4.1) that were sandy clay loam indicating higher clay contents of the area from the soil samples were obtained.

The soil pH in water ranged between 5.45 and 7.01, and this was rated acidic to neutral in all soil parent materials (Table 4.3) and are within the range of values (4.5 to 7.1) reported by Abdu (2006) for similar Nigerian savanna soils. Similarly, Raji and Muhammad (2000) also reported similar value for Nigerian savanna soils.

**Table 4.1 Particle – size distribution of selected soils developed over 3 parent materials**

Sampling location	Depth (cm)	Sand	Silt	Clay	Textural class
		← g / kg →			
<b>CHAD FORMATION (CF)</b>					
Digiza	0-15	744.00	185.60	106.40	Sandy loam
Digiza	15-30	648.60	223.70	127.70	Sandy loam
Gongo	0-15	824.00	85.80	86.40	Sandy loam
Gongo	15-30	808.00	104.10	87.90	Sandy loam
Guda	0-15	828.00	85.60	86.40	Sandy loam
Guda	15-30	817.00	87.10	95.90	Sandy loam
<b>BASEMENT COMPLEX ROCK (BCR)</b>					
Tawayla	0-15	688.00	225.60	86.40	Sandy loam
Tawayla	15-30	651.60	179.20	169.20	Sandy loam
Jaberi	0-15	817.40	94.80	87.80	Sandy loam
Jaberi	15-30	805.20	105.60	89.20	Sandy loam
Zenabari	0-15	808.00	105.60	86.40	Sandy loam
Zenabari	15-30	668.00	155.60	176.40	Sandy clay loam
<b>KERRI – KERRI FORMATION (KKF)</b>					
Kauyan Jalo	0-15	858.00	55.60	86.40	Sandy loam
Kauyan Jalo	15-30	808.00	105.60	86.40	Sandy loam
Doguwa	0-15	733.00	150.60	116.40	Sandy loam
Doguwa	15-30	713.00	165.60	121.40	Sandy loam
Kwari	0-15	678.00	195.60	126.40	Sandy loam
Kwari	15-30	618.00	175.60	206.40	Sandy clay loam

**Table 4.2 Selected physical and chemical properties of some soils developed from three different parent materials in northern Nigeria**

<b>Parameters</b>	<b>CF</b>	<b>BCR</b>	<b>KKF</b>
Sand (g / kg)	<b>778.30a</b>	<b>739.70a</b>	<b>6734.7a</b>
Silt (g / kg)	<b>128.70a</b>	<b>144.40a</b>	<b>141.40a</b>
Clay (g / kg)	<b>98.50a</b>	<b>115.90a</b>	<b>123.90a</b>
Texture	<b>SL</b>	<b>SL – SCL</b>	<b>SL – SCL</b>
pH in water	<b>6.54a</b>	<b>6.20b</b>	<b>5.86c</b>
pH in CaCl <sub>2</sub>	<b>5.48a</b>	<b>5.06b</b>	<b>4.84b</b>
Org. C (g / kg)	<b>5.30a</b>	<b>5.16a</b>	<b>5.37a</b>
Ca <sup>2+</sup> (cmol (+) / kg)	<b>2.04a</b>	<b>2.03a</b>	<b>2.19a</b>
Mg <sup>2+</sup> (cmol (+) / kg)	<b>0.70a</b>	<b>0.71a</b>	<b>0.64a</b>
K <sup>+</sup> (cmol (+) / kg)	<b>0.21a</b>	<b>0.22a</b>	<b>0.21a</b>
Na <sup>+</sup> (cmol (+) / kg)	<b>0.13a</b>	<b>0.13a</b>	<b>0.13a</b>
CEC (cmol (+) / kg)	<b>4.89a</b>	<b>4.44a</b>	<b>4.93a</b>
BS (%)	<b>63.27a</b>	<b>69.44a</b>	<b>65.49a</b>

CF= Chad Formation, BCR= Basement complex rock, KKF= Kerri-Kerri Formation, SL= Sandy loam, SCL= Sandy clay loam: Data presented are range with mean in parenthesis: Means within the same column having the same common small letter(s) are not significantly different at 5% from each other.

The predominant pH was slightly acidic (Table 4.3), except in soils developed over CF (Table 4.2) both values fell within range of soil pH for normal productive soils. The soil pH in CaCl<sub>2</sub> was lower compared to soil pH in water and the difference between pH in CaCl<sub>2</sub> to pH in water was negative and fairly large indicating dominance of variable charge minerals. The mean values of soil pH in water and CaCl<sub>2</sub> were significantly ( $p > 0.05$ ) different between soil parent materials (Table 4.2). Such differences are expected since the soils developed from different parent materials. This observation corroborates the findings of Jaiyeoba (2006) for soil that derived from different parent materials in Nigeria. The soils are low in organic carbon (Table 4.2), irrespective of soil parent materials. These low values are attributable to the high temperature and sometimes, moderate rainfall which accelerate rate of organic matter decomposition. This result was consistent with findings of several researchers (Yaro *et al.*, 2006; Mustapha *et al.*, 2007; Mulima *et al.*, 2015) for some soils of the Nigerian savanna. The mean values of organic carbon in all soils were not significantly different ( $p > 0.05$ ) indicating no influence of parent materials on organic carbon content of the soils.

The exchangeable Ca<sup>2+</sup> values ranged from 1.43 to 2.90 cmol<sub>(+)</sub>/kg in soils of all the three parent materials (Table 4.3), and this was rated low to moderate. These results are in line with findings of Hassan *et al.* (2016) in some soils elsewhere in the Northern Guinea savanna of Nigeria. Exchangeable Mg<sup>2+</sup> values in all the three parent materials were rated moderate, being greater than 0.3 cmol<sub>(+)</sub>/kg (Table 4.3) reported by Esu (1991) as the critical limit. The exchangeable K<sup>+</sup> values are generally rated moderate to high with higher values in soils derived from BCR and KKF (Table 4.3), but low value of 0.13 cmol<sub>(+)</sub>/kg was also obtained from soils developed over KKF (Table 4.3). Exchangeable Na<sup>+</sup> values ranged from 0.09 to 0.18 cmol (+) / kg are rated low to moderate (Table 4.3) in all the parent materials.

**Table 4.3 Selected chemical properties of some soils developed over three parent materials**

Location	Depth (cm)	pH in Water	pH in CaCl <sub>2</sub>	OC g / kg	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	CEC	BS %	
					←————— Cmol (+) / kg —————→						
<b>CHAD FORMATION (CF)</b>											
Digiza	0-15	6.73	5.65	5.95	2.51	0.75	0.22	0.17	5.99	60.93	
Digiza	15-30	6.63	5.39	4.40	1.73	0.60	0.18	0.15	4.94	54.23	
Gongo	0-15	6.15	5.18	5.71	2.35	0.76	0.23	0.12	4.84	71.10	
Gongo	15-30	6.02	5.08	3.75	1.70	0.58	0.17	0.12	4.24	60.37	
Guda	0-15	7.01	5.95	6.85	2.08	0.85	0.27	0.11	5.18	63.75	
Guda	15-30	6.80	5.64	5.15	1.88	0.67	0.22	0.11	4.16	69.23	
<b>BASEMENT COMPLEX ROCK (BCR)</b>											
Tawayla	0-15	6.37	4.83	6.80	2.80	0.99	0.33	0.10	5.10	82.80	
Tawayla	15-30	6.01	4.99	4.80	1.43	0.58	0.19	0.16	3.25	72.44	
Jaberi	0-15	6.18	5.21	4.50	1.97	0.69	0.20	0.12	5.09	58.83	
Jaberi	15-30	5.70	4.62	3.40	1.72	0.57	0.16	0.17	4.32	60.29	
Zenabari	0-15	6.58	5.47	7.25	2.44	0.96	0.28	0.10	4.82	78.55	
Zenabari	15-30	6.35	5.28	4.20	1.80	0.48	0.16	0.13	4.05	63.73	
<b>KERRI – KERRI FORMATION (KKF)</b>											
Kauyan Jalo	0-15	5.79	4.82	6.85	2.90	0.85	0.32	0.10	6.34	65.68	
Kauyan Jalo	15-30	6.06	5.16	4.60	1.86	0.57	0.19	0.15	4.16	66.32	
Doguwa	0-15	6.22	4.96	6.40	2.46	0.72	0.23	0.10	5.06	69.29	
Doguwa	15-30	5.95	5.10	4.70	1.59	0.44	0.13	0.16	4.06	56.19	
Kwari	0-15	5.72	4.50	6.75	2.59	0.60	0.25	0.09	5.70	69.15	
Kwari	15-30	5.45	4.49	2.90	1.76	0.67	0.18	0.18	4.18	66.36	

OC = Organic carbon



However, surface soils values for all exchangeable bases are higher than their corresponding sub-surface soils, irrespective of parent materials (Table 4.3). The cation exchange capacity (CEC) of the soils is rated low, being less than critical limit of  $6 \text{ cmol}_{(+)} / \text{kg}$  reported by Esu (1991) except for surface soils of Kauyan Jalo with moderate value of  $6.34 \text{ cmol}_{(+)} / \text{kg}$  on KKF (Table 4.3). Prolonged weathering and leaching of base cations, sandy nature of the soils, low colloidal activity (low organic matter) and clay mineralogy dominated by kaolinite and Al and Fe oxides of these soils in the three parent materials might be the reason for such low CEC.

The mean values of exchangeable bases ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$ ), and CEC in all the soils on three parent materials were not significantly different ( $p > 0.05$ ) (Table 4.2). The lack of significant differences might be due to the low organic matter content, sandy nature of the soil and generally the highly weathered nature of the soils. Base saturation values are rated moderate in all the soils, being greater than 50% reported by Esu (1991) as the critical limit except for soils on BCR with higher value of 82.80% (Table 4.2). These values of Base saturation of these soils indicate the dominance of the exchangeable bases over the exchangeable acidity. The mean values of Base saturation in all soils over the three parent materials are not significantly different ( $p = 0.05$ ) (Table 4.2).

Three fractions of iron (Fe) and aluminum (Al) oxides (dithionite citrate bicarbonate- Fed and Ald; oxalate-Feox and Alox; and sodium pyrophosphate-Fep and Alp) were determined in this study. The forms, contents and distribution of these oxides are important parameters for the proper understanding of the nature of S desorption in the soils. Consequently, the fate and transport of sulphate in soils is predominantly regulated by sorption reactions with Fe and Al oxides (Pauli *et al.*, 2006), making S unavailable in highly weathered tropical soils.

The values of Fed ranged from 5.78 to 59.35 g / kg across the soil parent materials (Table 4.4), and are close to values (8.7 to 38.10 g/kg) reported by Abdu (2006) on various soils of different parent materials and Maniyunda *et al.* (2015) that reported 5.7 to 34.86 g/kg for some soils that developed over basement complex rock, but differ than values (2.03 to 20.54 g/kg) obtained by Ajiboye *et al.* (2015) in Talc overburdened soils and Osodeke *et al.* (2005) that reported 6.0 to 74.9 g/kg in some soils in Umudike all in Nigeria. The values obtained here are also different significantly from the values (71.8 to 444.3 g/kg) reported by Olatunji *et al.* (2015) in soil that developed on basement complex rock in South Western Nigeria. These variations may be attributed to variations in climatic condition and soil water drainage. The Ald values ranged between 4.47 and 43.79 g /kg in all the soils from the three parent materials (Table 4.4). The values of Ald were higher than those (0.10 to 2.13 g /kg) reported by Abdu (2006) on various parent materials but lower than values (3.37 to 43.31 %) reported by Olatunji *et al.* (2015) on basement complex soils on some soils of Nigeria.

The acid ammonium oxalate extracts poorly crystalline Fe and Al from their oxides (Fe<sub>ox</sub> and Al<sub>ox</sub>). The amorphous iron oxides (Fe<sub>ox</sub>) in soils across the three parent materials varied from 1.03 to 33.87 g/kg (Table 4.4) and are within the values obtained by Amuri *et al.* (2012) ( 2.8 to 39.1 g/kg) for some soils of Mbeya region in Tanzania, but higher than values (0.25 to 1.12 g/kg) obtained by Abdu (2006) for soils of Nigerian savanna and Ajiboye *et al.* (2015) that reported 0.39 to 4.35 g/kg for Talc overburdened soils of Southern Guinea savanna of Nigeria. The values of Fe<sub>ox</sub> obtained were extremely lower than values (27.4 to 433.1 g/kg) obtained by Olatunji *et al.* (2015) on basement complex soil in South-Western Nigeria. While, the Ald values ranged from 0.31 to 27.26 g/kg in all the soils on various parent materials (Table 4.4).

**Table 4.4 Forms of iron (Fe) and aluminium (Al) oxides of some soils of different parent materials**

Sampling location	Depth (cm)	Fed	Ald	Feox	Alox	Fep	Alp	
		← g / kg →						
<b>CHAD FORMATION (CF)</b>								
Digiza	0-15	11.98	4.47	5.89	3.05	2.85	1.58	
Digiza	15-30	20.19	8.63	9.97	7.84	7.11	3.32	
Gongo	0-15	10.04	7.15	4.36	3.79	3.43	1.39	
Gongo	15-30	15.50	6.50	6.07	2.55	2.55	1.55	
Guda	0-15	5.78	1.37	1.03	0.31	0.45	0.34	
Guda	15-30	9.94	6.16	7.22	4.38	3.98	1.55	
<b>BASEMENT COMPLEX ROCK (BCR)</b>								
Tawayla	0-15	25.08	14.92	14.32	9.28	8.69	9.20	
Tawayla	15-30	49.84	34.40	26.15	19.88	16.58	6.65	
Jaberi	0-15	32.02	19.50	18.99	7.54	6.91	5.23	
Jaberi	15-30	52.12	34.12	33.87	27.26	18.43	11.62	
Zenabari	0-15	19.30	11.92	16.93	9.71	5.50	3.83	
Zenabari	15-30	59.35	43.79	27.95	22.21	14.24	8.96	
<b>KERRI – KERRI FORMATION (KKF)</b>								
Kauyan Jalo	0-15	21.18	8.66	6.62	4.29	3.43	1.83	
Kauyan Jalo	15-30	35.20	19.57	13.47	11.45	8.99	3.72	
Doguwa	0-15	14.26	12.67	11.93	5.96	6.77	2.94	
Doguwa	15-30	21.62	16.54	14.15	9.45	8.12	4.54	
Kwari	0-15	18.21	11.05	10.88	6.15	7.93	4.31	
Kwari	15-30	25.29	17.95	13.78	7.72	4.89	2.67	

These values were higher than values (0.15 to 0.40 g/kg) obtained by Abdu (2006) for Nigerian savanna soils, but very lower compared to values (13.0 to 86.6 g/kg) reported by Olatunji *et al.* (2015) on basement complex soil in South-Western Nigeria. The variation also might be related to difference in parent material, drainage condition, moisture regime and ecological zones of all the various studied soils. The oxalate extractable iron (Fe<sub>ox</sub>) and aluminum (Al<sub>ox</sub>) values generally lower than the dithionite extractable oxides for all the soils of the three different parent materials (Table 4.4), suggesting the dominance of crystalline Fe and Al over amorphous forms. This observation was also found by several other workers (Abdu, 2006; Samndi, 2012; Olatunji *et al.*, 2015) for Nigerian savanna soils. Since high amount of crystalline oxides is an indication of high degree of soil weathering (Jackson, 1964), then all of the studied soils can be categorized as highly weathered soils.

Sodium pyrophosphate extractable iron (Fe<sub>p</sub>) and aluminium (Al<sub>p</sub>) represent the organically bound form of Fe and Al of the soils (McKeague, 1967). The values of Fe<sub>p</sub> ranged from 0.45 to 18.43 g/kg in soils developed over the three parent materials (Table 4.4). The values obtained were higher than values reported by Raji *et al.* (2000) on ancient dunes soils in North- Western Nigeria. The values of Al<sub>p</sub> ranged between 0.34 to 11.62 g/kg in all the soils on the various parent materials (Table 4.4). The low value of pyrophosphate sesquioxides might be attributed to low organic matter contents of these soils (> 20g/kg) (Raji *et al.*, 2000).

The mean values of the different forms of oxides (Dithionite citrate bicarbonate- Fe and Al; Oxalate – Fe and Al; and Sodium pyrophosphate- Fe and Al) were significantly different ( $p > 0.05$ ) (Table 4.5), and this implies that the parent material has significant influence on forms, content and distribution of these oxides. The mean values of all the various forms of oxides of soils on BCR were significantly greater than KKF and CF. Soils on KKF were significantly

greater than CF. The variations might be attributed to difference in the compositions of the parent materials, modes of their formation, clay content, organic matter content and drainage conditions of these soils. The trend in magnitude of the various forms of oxides and parent materials respectively are as follows: Dithionite > Oxalate > Pyrophosphate and BCR > KKF > CF (Table 4.5). However, dithionite extracts (Fed and Ald), Oxalate (Feox and Alox) and pyrophosphate extracts (Fep and Alp) values were higher in sub-surface soils compared to their surface soils across the three parent materials (Table 4.4). This might be related to co-translocation of Fe and Al oxides with clay from surface to sub-surface soils through elluviations - illuviations processes (Blume and Schwertmann, 1969; Juo *et al.*, 1974; Samndi, 2012; Olatunji *et al.*, 2015). The pattern corresponds with distribution of colloidal materials (i.e. clay and organ carbon contents) in all the studied soils (Tables 4. 1 and 3).

The Al forms and content in all soils developed over three different parent materials was lower than the forms and content of Fe oxides (Table 4.5), suggesting that Al is not as important as Fe in inhibiting of sulphate desorption. A similar trend was noted by Singh (1984) and Stanko-Golden *et al.* (1994). They noted that the extraction procedure for Fe also releases Al so that levels of Fe might be overestimated. This phenomenon might also be true for the forms and content of sesquioxides in the soils in this study. However, abundance of ferromagnesian minerals in the soils of the Nigerian savanna might be another reason for having higher Fe content in all studied soils, and similar observation was made by several researchers (Samndi, 2012; Maniyunda *et al.*, 2014; 2015; Olatunji *et al.*, 2015).

**Table 4.5 Mean concentration of forms and content of sesquioxides iron and aluminum and sulphur of some soils that developed from three different parent materials**

<b>Parameters</b>	<b>CF</b>	<b>BCR</b>	<b>KKF</b>
Fed (g / kg)	<b>12.65c</b>	<b>39.62a</b>	<b>22.63b</b>
Ald (g / kg)	<b>5.71c</b>	<b>24.44a</b>	<b>14.40b</b>
Feox (g / kg)	<b>5.75c</b>	<b>23.03a</b>	<b>11.80b</b>
Alox (g / kg)	<b>3.98b</b>	<b>15.98a</b>	<b>7.50b</b>
Fe p (g / kg)	<b>3.39b</b>	<b>11.72a</b>	<b>6.69b</b>
Alp (g / kg)	<b>1.62c</b>	<b>7.58a</b>	<b>3.34b</b>
T.S (mg / kg)	<b>246.4a</b>	<b>149.70b</b>	<b>182.20ab</b>
Org. S (mg / kg)	<b>198.80a</b>	<b>119.5b</b>	<b>141.10ab</b>
In. S (mg / kg)	<b>46.82a</b>	<b>30.20a</b>	<b>41.06a</b>

CF= Chad formation, BCR= Basement complex rock, KKF= Kerri-Kerri formation: Data presented are range with mean in parenthesis: Mean values with same letter (s) in the horizontal column are not significantly different from one another at  $p < 0.05$

## 4.2 Sulphur status of the study soils

The different forms of soil sulphur in the soils of the various parent materials are shown in Table 4.2. The total sulphur (TS) values in all the studied soils on the various parent materials ranged from 77.91 to 501.19 mg/kg (Table 4.6), and are similar to the values (117 to 489 mg/kg) obtained by Kang *et al.* (1981) for forest zones soils and Raji (2008) that reported a range of 97 to 489.38 mg/kg for sand dune soils, all for Nigerian savanna soils. These values also are in line with the ranges (43 to 398 mg/kg) reported by Tabatabai (2005a) and a range of 55 to 580 mg/kg in Brazilian and Iowa soils respectively. However, values of total sulphur in this study are lower compared to values (520 to 1082 mg/kg) reported by Solomon *et al.* (2001) for Ethiopian soils. The differences in organic matter contents, climatic conditions, depth of soil sampling and parent materials may account for the varying of total sulphur content (Solomon *et al.*, 2001; Tabatabai, 2005a; Raji, 2008). The values of total sulphur in all the studied soils are generally low and similar observation made by Kang *et al.* (1981) and Raji (2008) for Nigerian savanna soils, while Buri *et al.* (2000) for soils of West African lowlands. These deficient values of total sulphur are attributable due to low organic matter contents and sandy nature of West African soils.

The mean values of total sulphur in all soils from three parent materials were significantly different ( $p > 0.05$ ) (Table 4.5), and this implied that the parent materials had significant influenced on contents and distribution of total sulphur. In order of magnitude the total sulphur in soils of different parent materials could be arranged as follows:  $CF \geq KKF \geq BCR$  (Table 4.5). This trend corroborated the observation of Bowen (1966) and Friend (1973) as follows: parent materials contain varying amounts of S following the increasing trend in igneous rocks < metamorphic rocks < magmatic rocks << limestone < sedimentary rocks (sulphides) < shales < sedimentary rocks (sulphates) << coal.

**Table 4.6 Selected forms of sulphur of some soils developed over 3 parent materials**

Sampling location	Depth (cm)	Total Sulphur	Organic Sulphur	Inorganic Sulphur
		mg / kg		
<b>CHAD FORMATION (CF)</b>				
Digiza	0-15	501.19	377.41	123.78
Digiza	15-30	275.13	230.60	44.53
Gongo	0-15	240.82	206.19	29.63
Gongo	15-30	222.37	190.08	32.29
Guda	0-15	127.08	97.12	29.96
Guda	15-30	111.93	91.19	20.74
<b>BASEMENT COMPLEX ROCK (BCR)</b>				
Tawayla	0-15	233.60	197.20	36.40
Tawayla	15-30	77.91	57.53	20.38
Jaberi	0-15	201.68	144.31	57.37
Jaberi	15-30	107.54	86.37	21.17
Zenabari	0-15	190.89	167.12	23.77
Zenabari	15-30	86.66	64.54	22.12
<b>KERRI – KERRI FORMATION (KKF)</b>				
Kauyan Jalo	0-15	388.85	317.01	71.85
Kauyan Jalo	15-30	104.43	80.62	23.84
Doguwa	0-15	251.82	180.48	71.32
Doguwa	15-30	107.13	75.81	31.33
Kwari	0-15	142.48	112.75	29.73
Kwari	15-30	98.26	79.93	18.33



The reason for differences might be attributed to the differences in parent materials and modes of their formation as well as Fe and Al oxides. However, the values of total sulphur in all surface soils on the various parent materials were higher than their corresponding sub-surface soils (Table 4.6). This might be due to the fact that sulphur occurs principally in organic form (Tabatabai, 2005a), which is normally higher in the surface horizons (Raji, 2008).

The organic sulphur (Org. S) values in all three parent materials ranged from 57.53 to 377.41 mg/kg (Table 4.6), and are similar to the values obtained by Tabatabai (2005a) in Brazilian and Iowa soils respectively, but lower than values obtained by Solomon *et al.* (2001) in Ethiopian soils. The variation might be due to differences in parent materials, climate and depth of soil sampling. The values of organic sulphur in all studied surface soils were higher compared to their corresponding sub-surface soils (Table 4.6), and the trend was similar to the pattern of organic carbon distribution (Table 4.3). The mean values of organic sulphur were significantly different ( $p > 0.05$ ) by soil parent materials (Table 4.5), and this revealed that the parent materials has significant influence on content and distribution of organic sulphur. The variations might be due to differences in parent materials and modes of their formation. In terms of order of magnitude, the mean values of organic sulphur in all soils from parent materials could be arranged as follows:  $CF \geq KKF \geq BCR$  (Table 4.5).

The values of inorganic sulphur (Org.S) ranged from 18.33 to 123.78 in all the soils across three parent materials, however the mean values were not significantly different ( $p > 0.05$ ) (Table 4.6). The lack of difference might be attributed to the old and highly weathered nature of tropical soils.

### 4.3 Influence of Parent Material on Kinetics Desorption of Sulphate

The amount of sulphate desorbed at different time intervals are shown in Figure 4.1. Desorption of the adsorbed  $\text{SO}_4^{2-}$  from the soils decreased with increasing contact time to all studied soils developed over three parent materials (Figure 4.1). Similarly, Ghosh and Dash (2012) reported decreased amount of desorbed sulphate with increasing time, particularly at higher temperatures because of conversion to a more tightly held form. A similar effect was also noted by Koopmans *et al.* (2004b) where desorption of phosphate decreased with increasing shaking time. Therefore, they suggested that the increase of shaking time caused abrasion of soil particles leading to the exposure of new surface sites and greater sorption. This situation might be true for decreased amount of desorbed sulphate with increasing time in this study. The contact time for extraction of S adsorbed from soil matrix (Solid and Solution phase) influences the degree and magnitude of S desorption. Consequently, time dependency of S desorption in agricultural soils are clearly critically important in understanding the efficiency with which plant roots absorb the nutrients from soil solution and leaching of sulphate by soils. The shaking time of 30 minutes was considered to be a good contact time for describing S desorption maxima in all the studied soils (Appendix 1).

Initially, desorption was rapid with > 65% being desorbed in 30 minutes (Appendix 2) in all soils developed over three different parent materials is consistent with findings by previous workers (Singh, 1984b; Sharpley, 1990; Garg *et al.*, 2016). After, the initial rapid desorption, the release of sulphate slowed down up to 240 minutes which has been attributed due to the diffusion into micro pores of inorganic minerals and into humic substances. A number of investigations have shown that sorption – desorption is characterized by a rapid reaction followed by a much slower reaction (Sparks, 2002, 2005; Borda and Sparks, 2008) or biphasic kinetics.

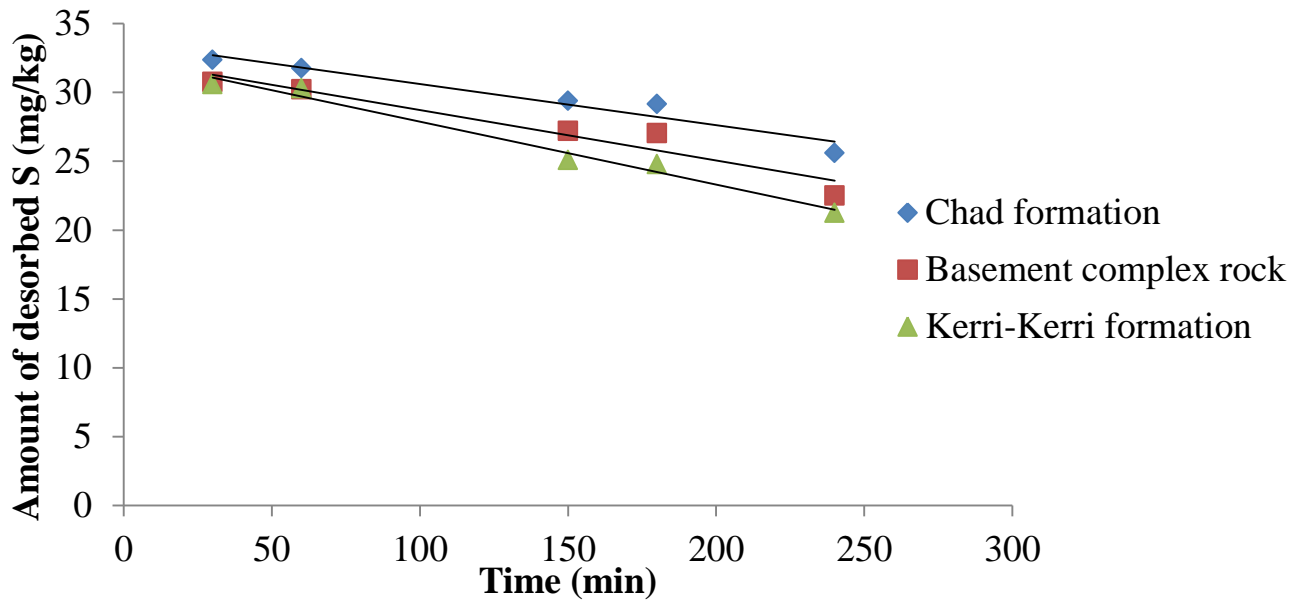


Figure 4. 1. Amount of desorbed sulphate at different time intervals by soil parent materials

This might reflect a heterogeneity nature of the soils. In some cases, probably due to contamination of solution with CO<sub>2</sub>, the effect enhance H<sup>+</sup> with resultant decreased in pH (Churchman and Lowe, 2012), and therefore, in such cases the amount of sulphate desorbed declined with increasing time.

In addition, the rapid phase of sulphate desorption has been attributed to retention of added sulphate in a labile form that is easily desorbed at initial contact time; however as time increases the amount of desorbed sulphate decreases accordingly because of entrapment of the sulphate in a non-labile form that is difficult to desorb. This slower sulphate desorption has been described to diffusion of the added sulphate into micropores of organic and inorganic soil components. Equilibrium of sulphate desorption was attained at 150 minutes of equilibration in all studied soils as at 180 and 240 minutes of equilibration time of sulphate desorption was almost similar to that at 150 minutes (Appendix 1).

The difference between the amount of sulphate desorbed and adsorbed (Appendix 1) reflects the extent of irreversibility for a given SO<sub>4</sub><sup>2-</sup> concentration in soil solution. This discrepancy between sorption and desorption pathways is often referred to as hysteresis. Similar findings have been made in other countries such as India (Reddy *et al.*, 2001; Sammi *et al.*, 2001; Ghosh and Dash, 20014) and Malawi (Maida and Navilata, 2016). However, the trend of distribution of amount of desorbed sulphate was contrary with forms of oxides (Table 4. 4) and clay fractions (Table 4.1), but similar with organic carbon and soil pH distributions (Table 4.3). This may reflect the abundances of Fe and Al oxides and clay fraction dominated by kaolinite in sub-soils which in turn cause lower desorption. However, the amount of sulphate desorbed (Figure 4.1) and desorbed percentage (Appendix 2) were arranged in order of magnitude by soil parent materials

as follows: CF>BCR>KKF. Such fundamental differences in these parent materials may account for the varying degree and magnitude of sulphate desorption in these soils.

#### **4.3.1 Chad Formation**

The mean concentration of sulphate desorbed at different time intervals in all soils ranged from 25.60 to 32.37 mg/kg with an overall mean of 29.66 mg/kg (Figure 4.1). The highest mean value achieved at 30 minutes is consistent with previous findings (Singh, 1984b; Sharpley, 1990; Garg *et al.*, 2016)). Guda surface soils recorded highest concentration of sulphate desorbed which varied from 28.74-34.96 mg/kg at different contact times is attributable to the soil pH and organic matter content (Table 4.3). The lowest values ranged from 23.41 to 30.04 mg/kg in different time intervals were recorded in Gongo sub-soil. This could be the results of the lower soil pH and organic matter content by this soil (Table 4.3). The percentage of average means of the concentration of sulphate desorbed in all 6 soils was 71.62 %, while approximately 78.2% of the mean value of sulphate desorbed was released during the first initial 30 minutes of the reaction (Appendix 2). Similar observation was made by Barrow and Shaw (1977), Singh (1984b) and Sharpley (1990). This indicates the biphasic nature of the kinetic desorption of sulphate at different time intervals. Diffusion into soil microspore has been suggested as one reason for slow reaction times (Sparks, 2002; 2005) after initial desorption time of 30 minutes.

#### **4.3.2 Basement Complex rock**

The mean concentration of sulphate desorbed at different time intervals in all studied soils are presented in Figure 4.1. It ranged from 22.50 to 30.76 mg/kg with an overall mean of 27.62 mg/kg (Figure 4.1) for all six locations. The highest value (32.08 mg/kg) of sulphate desorbed was observed in Zenabari forest top-soils (Appendix 1). Because sulphate desorption in soils has

been reported to be more extensive in soils that are higher in soil pH (Table 4.3), particularly in surface soils. The influence of Al and Fe is lower at a higher soil pH in this soil. The level of organic carbon may also be another reason for having highest desorption value in this soil.

The means percentage of concentration of sulphate desorbed ranged from 52.51 to 71.77% (Figure 4.1) in all studied soils. The pattern of sulphate desorbed was similar to those in soil developed over CF. However, sulphate desorption in these soils were lower than sulphate desorbed from soils developed over CF. Consequently, soils with a low Fe and Al oxides contents release more adsorb sulphate into soil solution than soils with high Fe and Al oxide contents (Tabatabai, 2005a; Ghosh and Dash, 2012).

### **4.3.3 Kerri-Kerri Formation**

Sulphate desorption from soils that developed over KKF followed the same pattern as soils that developed over BCR and CF. Desorption was greater in grassland soils in Dogowa (Figure 4.1) with a higher soil pH (Table 4.3). The lower value (28.94 mg/kg) of sulphate desorbed was recorded from Kwari sub-soils are attributable to low level of soil pH and organic matter (Table 4.3). The percentage mean concentration of sulphate desorbed in all soils ranged from 50.51 to 72.65% with an overall mean of 63.10% (Appendix 2). The magnitude order of sulphate desorption from soils developed over three different parent materials could be arranged as follows: CF > BCR > KKF. This trend could be attributed due to differences in parent materials and modes of their formation, which resulted in having different soil characteristics.

#### **4.4 Comparison of Kinetic Models to Describe Sulphate Desorption of Soils Derived from Different Parent Materials**

The model with appreciable  $R^2$ , but higher in standard errors (SE) is not a better model to describe experimental data (Abdu, 2006; Rezaei and Naeini, 2009; Brajendra *et al.*, 2013; Garg *et al.*, 2016). The kinetic equations along with values of coefficient of determination ( $R^2$ ) and standard errors (SE) of soils derived from three different parent materials are presented in Table 4.3. The ordered or mechanistic models (First-order and second -order) and diffusional models (Elovich, Fractional-power and parabolic diffusion equations) were used to compare the best fit to the experimental data that satisfactorily describe the sulphate desorption data.

##### **4.4.1 Ordered or Mechanistic models**

The first-order was the best in all studied soils to describe the reaction rate of S desorption data as evidenced by the overall highest values of  $R^2$  and the lowest values of SE (Table 4.7). This observation conforms to findings of previous workers on sulphate desorption data (Abdu *et al.*, 2008; Brajendra *et al.*, 2013; Garg *et al.*, 2016). Goodness of fit of first-order equation on sulphate desorption data from soils derived from the three different parent materials was in the order as follows: CF>BCR>KKF. This trend was also similar to the trend of order of amount of sulphate desorbed by soil parent materials. The variations might be attributed to differences in soil pH, clay content, and forms and content of Fe and Al oxides. Conformity of this experimental data to first order equation is an indication of a probable ligand exchange of sulphate ion during the desorption process (Abdu *et al.*, 2008; Abdu, 2013).

**Table 4.7: Coefficient of determination ( $R^2$ ) and standard error of estimate (SE) of various kinetic equations for sulphate desorption in some soils developed over different parent materials**

Equation	Parent material					
	CF		BCR		KKF	
	$R^2$	SE	$R^2$	SE	$R^2$	SE
First-order	0.9147	0.34	0.9207	0.76	0.976	0.93
Second-order	0.8938	3.53	0.8741	3.46	0.9649	8.28
Elovich	0.7994	2.60	0.7882	2.34	0.8953	1.99
Fractional power	0.7698	3.60	0.7499	3.37	0.8725	3.26
Parabolic diffusion law	0.876	0.00013	0.8678	0.00013	0.954	0.00082

CF= Chad formation, BCR= Basement complex rock, KKF= Kerri-Kerri formation



The second-order equation is not suitable to describe S desorption in all the studied soils as can be seen from the large values of SE compared to first-order equation, even though the  $R^2$  values are quite high. Similar observations were reported by Abdu (2013) for phosphate desorption data, and also by Brajendra *et al.* (2013) and Garg *et al.* (2016) for sulphate release data.

#### **4.4.2 Empirical models**

The parabolic diffusion, fractional power and the Elovich models have been regarded as empirical kinetic models (Abdu, 2006). The kinetic of S desorption in all studied soils derived from three different parent materials was also best described by the parabolic diffusion equation (Table 4.7) as characterized by relatively high  $R^2$  values and low SE values. This observation suggests intra-particle diffusion-controlled exchange in all studied soils. This was also found by Garg *et al.* (2016) for sulphate release data from Alfisols soils in India, and Abdu (2006) for phosphate release data in Nigerian savanna soils.

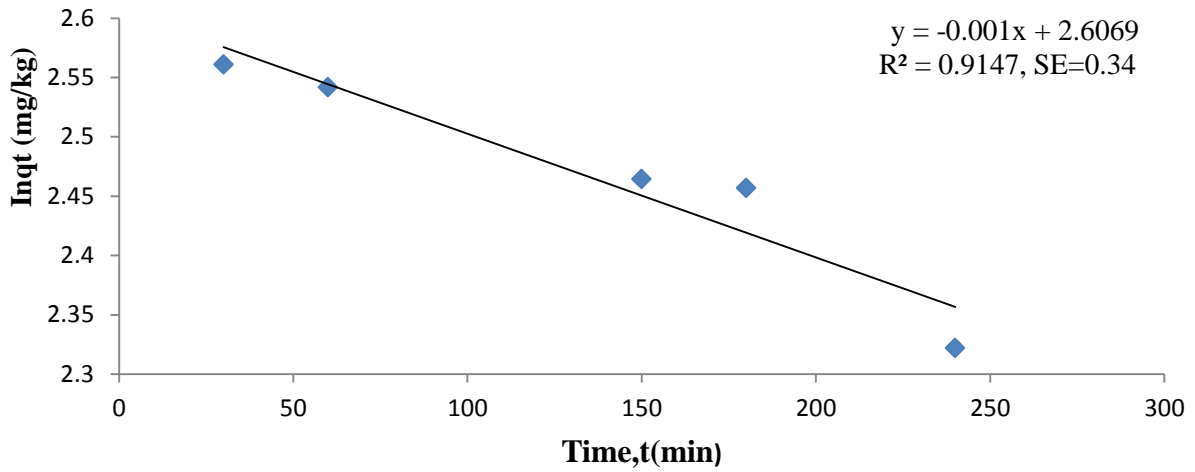
Both Elovich and fractional-power equations failed to successfully describe S desorption data in this study as can be seen from their large values of SE, though they have appreciable  $R^2$  (Table 4.7) by soil of all the different parent materials. This was contrary to the findings of Abdu (2006) on phosphate release data in soils from the Nigerian savanna. Work by Brajendra *et al.* (2013) on kinetics of sulphate release by soils showed that Elovich was not suitable to describe S desorption by soils as characterized by the large values of SE.

A comparison between best fit kinetic equations (First-order and parabolic diffusion models) by soils that developed over three parent materials showed that the parabolic diffusion equation could fit the sulphate desorption data better than first-order equation, as can be seen from the lowest values of SE (Table 4.7). Conformity of S desorption data to the parabolic diffusion

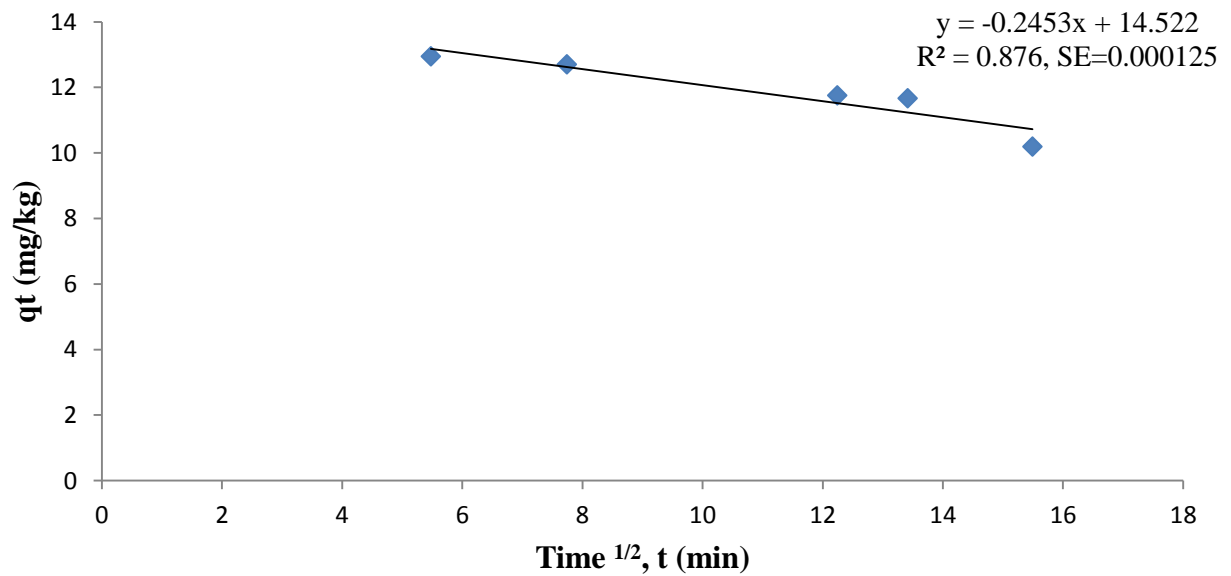
equation suggested that S released from the all studied soils may be consistent with diffusion-controlled transport phenomena or probably with the rate-limiting. This diffusion layer is probably the stagnant water film surrounding the soil particles or the intra – particles or water films on surfaces within the particles itself. Film diffusion was maintained by continuous shaking during experiment (Sparks *et al.*, 1980).

Therefore, Many authors speculated that the rate-controlling step in the adsorption or desorption of nutrients was the diffusion of the ions into the subsurface layers of the solid matrix (Sivasubramanian and Talibudeen, 1972; Agbenin and Raij, 2001; Abdu, 2006, 2009; Abdu *et al.*, 2008). However, in view of  $R^2$  and SE of the first-order model, it seems to be good for describing S desorption data.

The results of fitting a first-order and parabolic diffusion equations to desorption data are also illustrated in Figure 4.2, with the values of  $R^2$  and SE.



**Figure 4.2.1. Plot of first order for describing desorption data from soils developed over Chad Formation (CF)**



**Figure 4.2.2. Plot of parabolic-diffusion for describing desorption data by soils Chad Formation (CF)**

Cont.

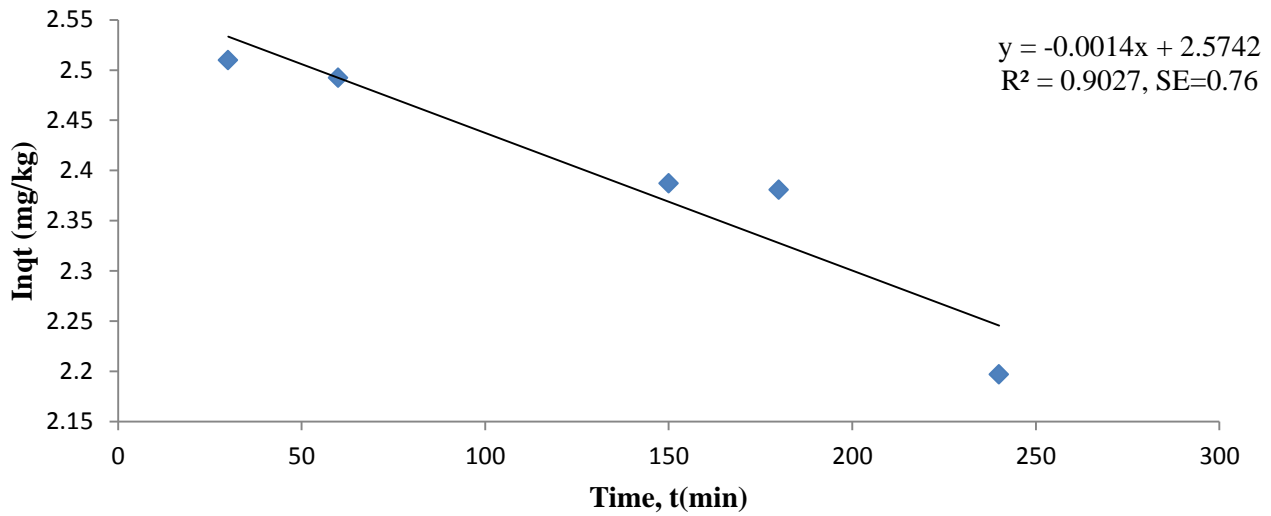


Figure 4.2.3. Plot of first order for describing desorption data by soils Basement complex rock (BCR)

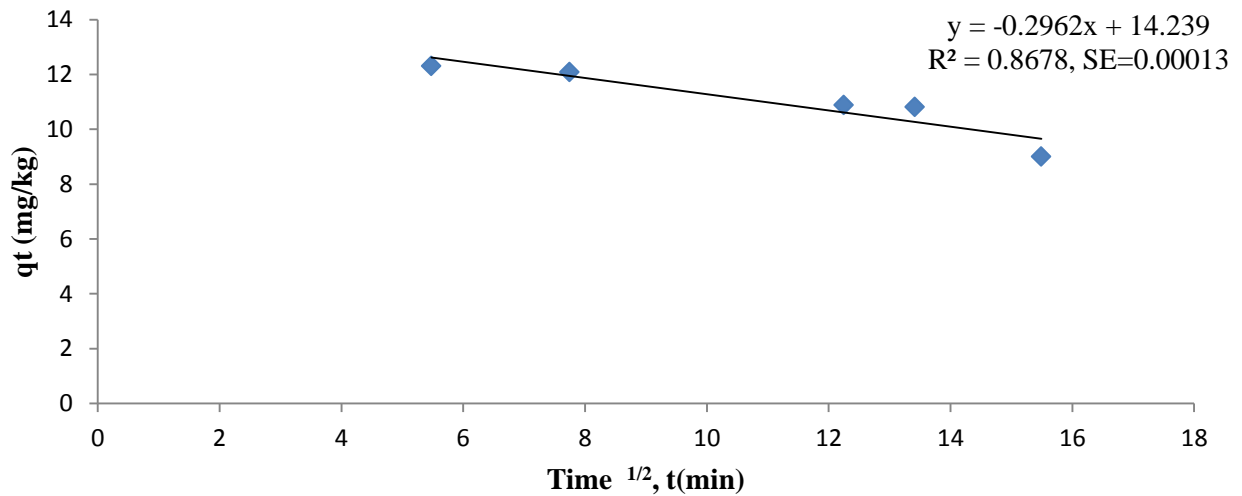


Figure 4.2.4. Plot of parabolic-diffusion for describing desorption data by soil Basement complex rock (BCR)

Cont.

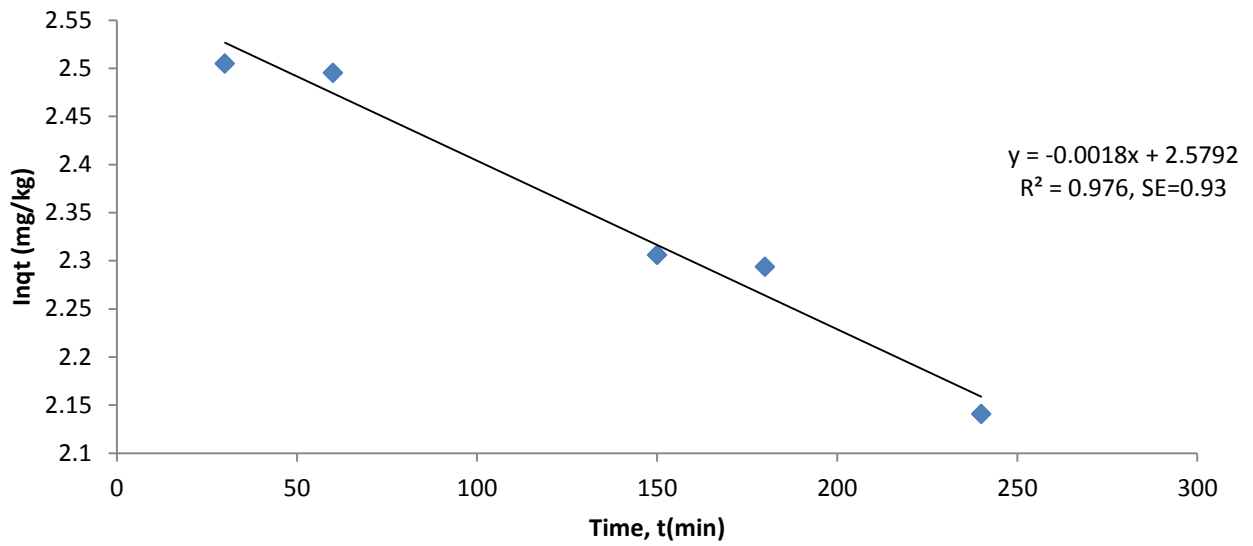


Figure 4.2.5. Plot of first order for describing desorption data by soils Kerri-Kerri Formation (KKF)

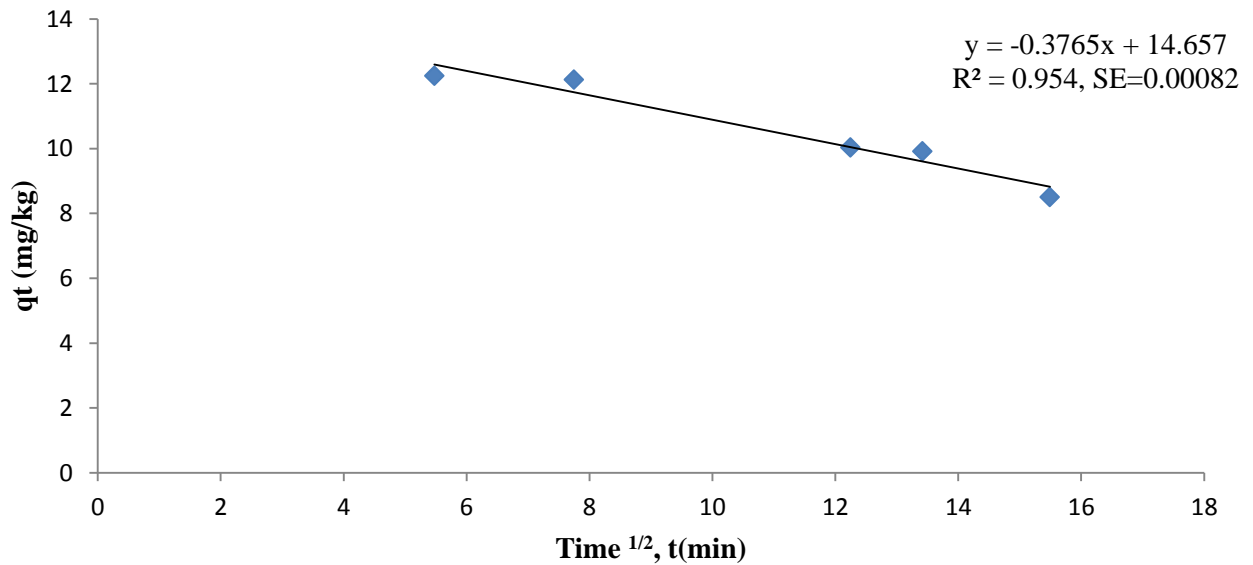


Figure 4.2.6. Plot of parabolic-diffusion for describing desorption data by soil Kerri-Kerri Formation (KKF)

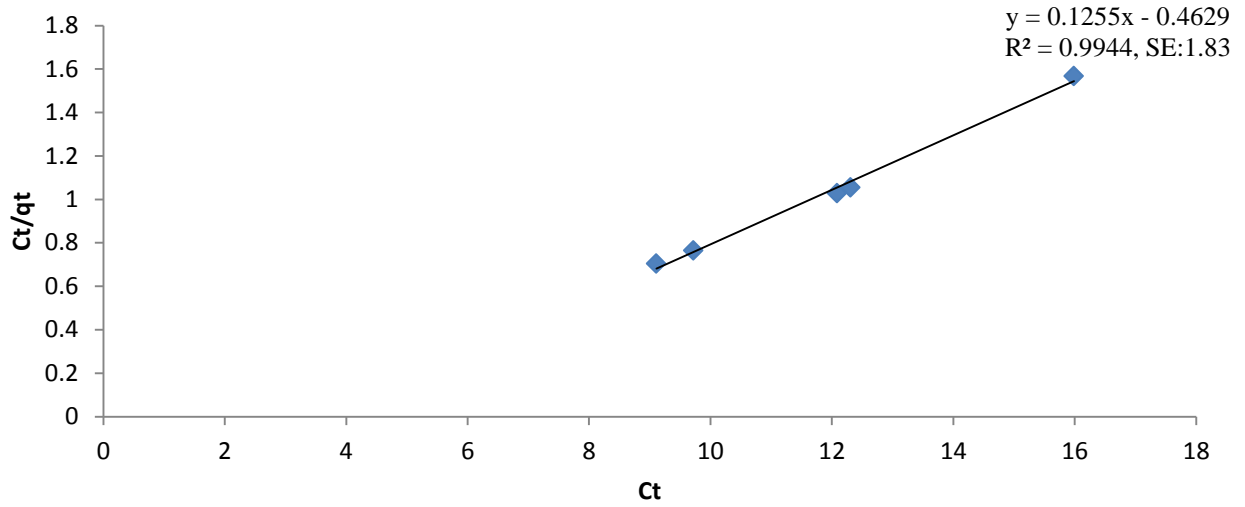
#### 4.5 Fitting Kinetic Data to Desorption Isotherms

The modeling of agricultural systems has brought significant improvements to farm productivity and also has raised awareness of environmental concerns (McCray *et al.*, 2005; Cichota, 2007). The goodness of fit of isotherm equations (Langmuir and Freundlich) to the desorption data obtained from soils developed over three different parent materials in Bauchi Sudan savanna are presented in Table 4.8 and Figure 4.3. Comparison of  $R^2$  values of the best isotherm equations indicated that both Langmuir and Freundlich isotherm models were suitable to describe S desorption data in all studied soils, as can be seen from  $R^2$  greater than 0.98. However, in view of the low SE, Langmuir equation gave a better fit to experimental data in this study (Table 4.8). This observation is in conformity with the other studies (Shailaya, 1989; Koopmans *et al.*, 2004b) that used these sorption models in describing P desorption data. No efforts have been made to test applicability of these isotherm equations to describe S kinetic desorption data by soils and soil components. The fit of experimental data to the Langmuir equation is an indication that desorption of sulphate into soil solutions is described adequate by the model. A good fit of this isotherm equation reflects monolayer desorption. Similarly, many soil chemists have successfully applied the Langmuir isotherm model to describe S adsorption in soils and soil components (Ajwa and Tabatabai, 1997; Lusk, 1998; Osodeke and Ubah, 2006; Farahmand *et al.*, 2015; Maida and Nalivata, 2016).

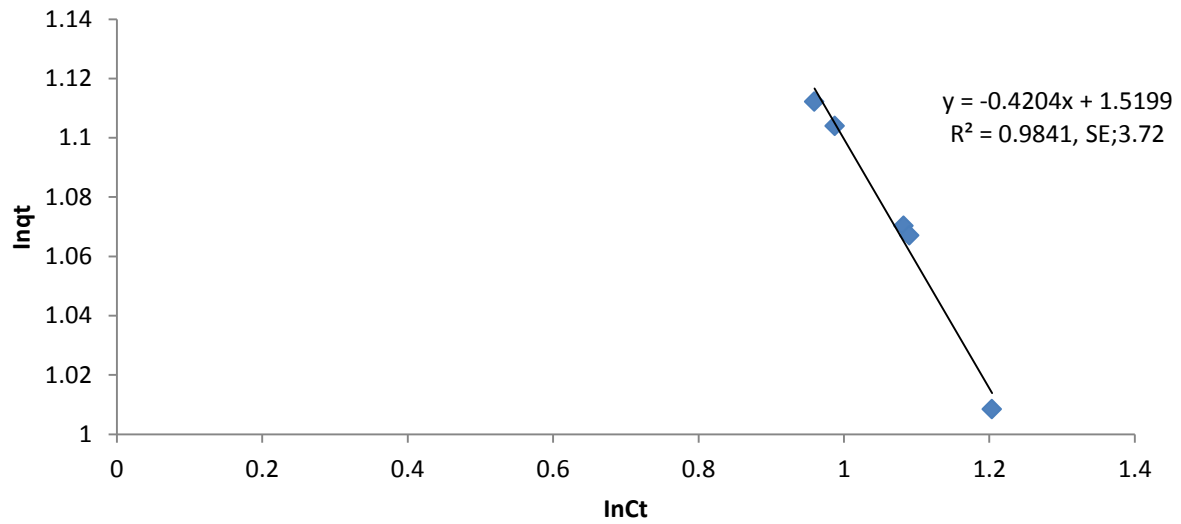
**Table 4.8: Coefficient of determination ( $R^2$ ) and standard error of estimate (SE) of various isotherm equations for sulphate desorption in some soils developed over different parent materials**

Isotherm equation	Parent material					
	CF		BCR		KKF	
	$R^2$	SE	$R^2$	SE	$R^2$	SE
Langmuir	0.9944	1.83	0.9906	1.995	0.9882	1.86
Freundlich	0.9841	3.72	0.9829	3.46	0.9832	3.32

CF= Chad formation, BCR= Basement complex rock, KKF= Kerri-Kerri formation



**Figure 4.3.1. Plot of Langmuir isotherm for describing desorption data by soil Chad Formation (CF)**



**Figure 4.3.2. Plot of Freundlich isotherm for describing desorption data by soil Chad formation (CF)**



Cont.

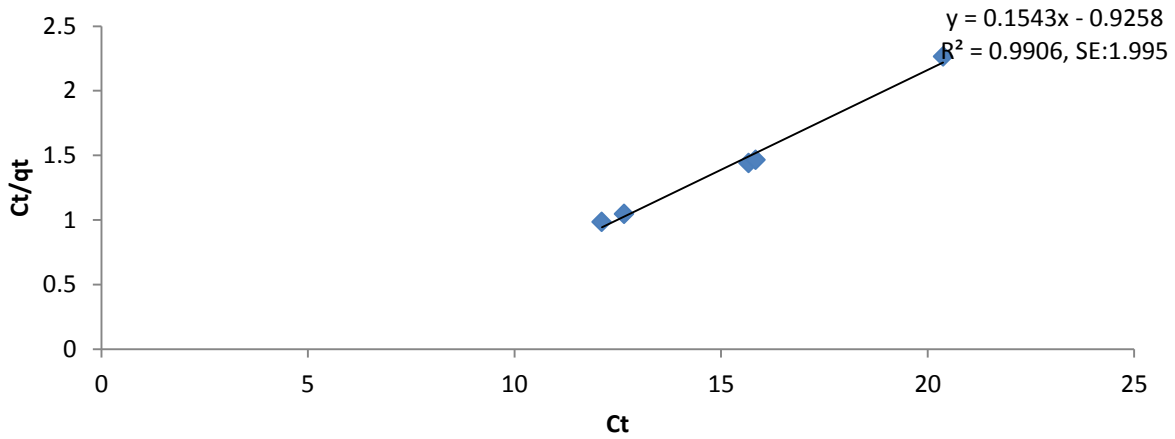


Figure 4.3.3. Plot of Langmuir isotherm for describing desorption data by soil Basement complex rock (BCR)

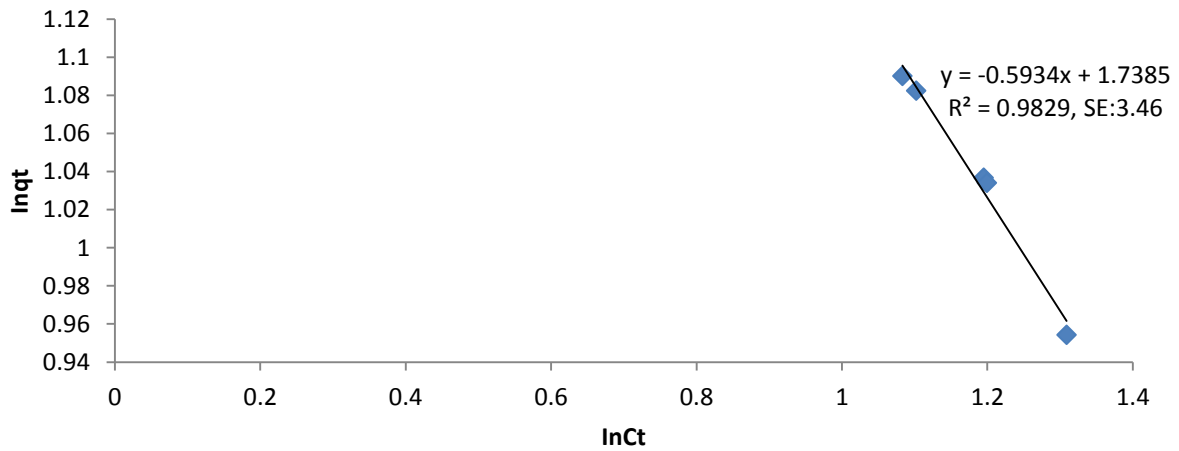
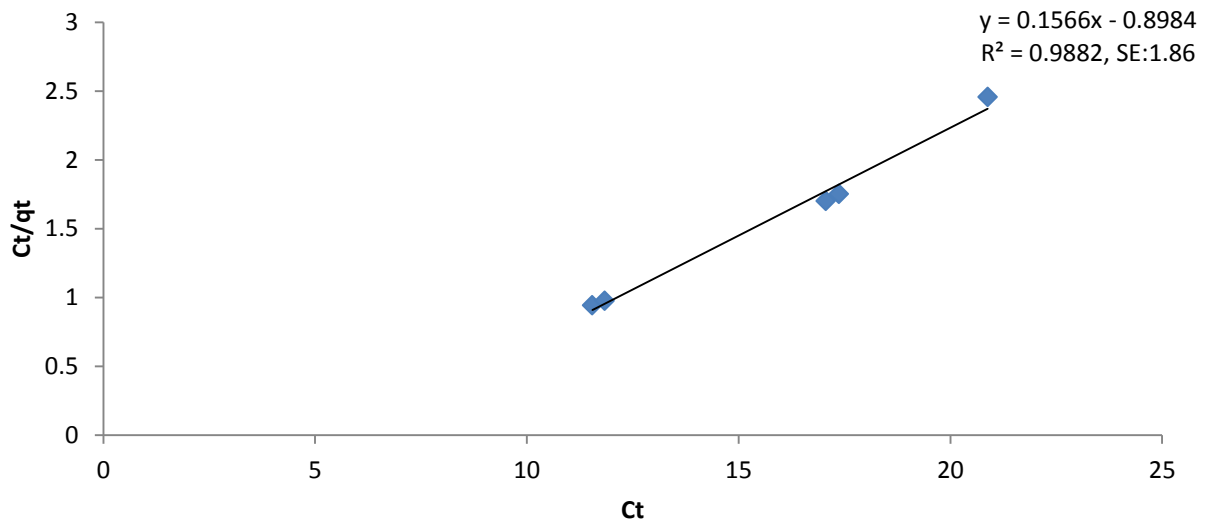
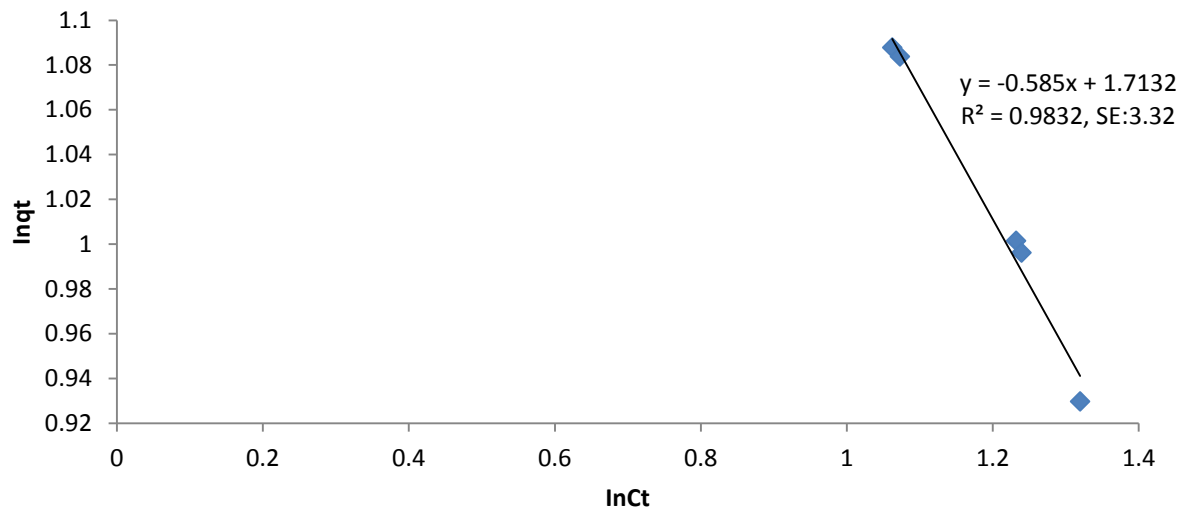


Figure 4.3.4. Plot of Freundlich isotherm for describing desorption data by soil Basement complex rock (BCR)

Cont.



**Figure 4.3.5. Plot of Langmuir isotherm for describing desorption data by soil Kerri- Kerri Formation (KKF)**



**Figure 4.3.6. Plot of Freundlich isotherm for describing desorption data by soil Kerri-Kerri Formation (KKF)**

## 4.6 Relationship between Sulphate Desorption Kinetic Parameters and Soils Properties Derived from Different Parent Materials

### 4.6.1 Chad Formation

Table 4.9 shows correlations between kinetic parameters and soil properties from soils derived from Chad formation. First-order rate constant ( $k_1$ ) correlated negatively and significantly with sand content (-0.999\*) and base saturation (BS) (-0.997\*). First-order constant ( $q_0$ ) was also negatively and significantly correlated with Na (-1.000\*). Fractional power constant ( $n_{fp}$ ) correlated negatively and significantly with sand contents (-0.999\*) and base saturation (BS) (-0.997\*). This suggested that the first-order modeling of S desorption data is inversely related to above soil properties. Silt content had a positive significant correlation with first-order rate constant ( $k_1$ ) (0.998\*) and fractional power rate constant ( $n_{fp}$ ) (0.999\*). This implies that as silt content increase the S desorption modeling by these kinetic rate constants of first order ( $k_1$ ) and fractional power ( $n_{fp}$ ) will be increased. There was positively and significantly correlation between soil pH and second-order  $q_e$  (0.997\*). Similarly, Freundlich constant ( $k_f$ ) correlated positively and significantly with soil pH (1.000\*). This is expected because at higher pH values S adsorption might decline due to the partial dissolution of Fe and Al oxides leading to destruction of sorption sites and thus augmenting S desorption in soils. Langmuir constant ( $k_L$ ) was positively and significantly correlated with organic carbon (0.998\*). This reflects the fact that sulphate has a lower binding energy than organic acids and, therefore, increase in organic matter result in the formation of organic acid-metal complex responsible for augmenting of S desorption in soils. A similar observation was made by Lusk (1998) and Maida and Navilata (2016) all for sulphate adsorption by soils.

**Table 4.9: Correlation between kinetic parameters and soil properties of soils derived from Chad formation (CF)**

	<b>k<sub>1</sub></b>	<b>q<sub>0</sub></b>	<b>k<sub>2</sub></b>	<b>q<sub>e</sub></b>	<b>B</b>	<b>a</b>	<b>n<sub>fp</sub></b>	<b>k<sub>fp</sub></b>	<b>R</b>	<b>b</b>	<b>q<sub>max</sub></b>	<b>k<sub>L</sub></b>	<b>n<sub>f</sub></b>	<b>k<sub>f</sub></b>
<b>Sand</b>	-0.999*	-0.993	-0.929	-0.125	0.720	-0.619	-0.999*	-0.435	-0.467	-0.118	0.069	0.279	-0.058	-0.022
<b>Silt</b>	0.998*	-0.995	0.922	0.106	-0.706	0.604	0.999*	0.417	0.450	0.099	-0.088	-0.298	0.039	-0.203
<b>Clay</b>	0.992	-0.959	0.978	0.290	-0.827	0.743	0.992	0.580	0.610	0.284	0.100	-0.113	0.1226	-0.383
<b>pH</b>	0.246	-0.085	0.549	0.997*	-0.825	-0.894	0.246	0.970	0.960	0.996	0.963	0.885	0.990	-1.000*
<b>Or.C</b>	-0.166	0.324	0.166	0.944	-0.527	0.637	-0.166	0.789	0.766	0.946	0.990	0.998*	0.964	-0.906
<b>Ca</b>	0.936	-0.981	0.769	-0.188	-0.470	0.346	0.936	0.135	0.171	-0.195	-0.374	-0.562	-0.253	0.906
<b>Mg</b>	-0.410	0.553	-0.088	0.829	-0.295	0.421	-0.410	0.608	0.578	0.833	0.921	0.983	0.865	-0.770
<b>K</b>	-0.655	0.769	-0.371	0.633	-0.008	0.143	-0.655	0.354	0.319	0.639	0.771	0.888	0.684	-0.554
<b>Na</b>	0.982	-1.000*	0.866	-0.019	-0.613	0.500	0.982	0.301	0.335	-0.026	-0.212	-0.414	-0.086	-0.080
<b>CEC</b>	0.992	-0.957	0.979	0.296	-0.830	0.747	0.992	0.585	0.614	0.289	0.106	-0.107	0.231	-0.389
<b>BS</b>	-0.997*	0.996	-0.917	-0.095	0.699	-0.595	-0.997*	-0.407	-0.440	-0.088	0.099	0.308	-0.028	0.193
<b>Fed</b>	0.805	-0.891	0.567	-0.447	-0.213	0.079	0.805	-0.139	-0.103	-0.453	-0.611	-0.765	-0.506	0.357
<b>Ald</b>	0.427	-0.568	0.107	-0.819	0.277	-0.404	0.427	-0.593	-0.563	-0.823	-0.914	-0.997	-0.885	0.758
<b>Feox</b>	0.960	-0.993	0.816	-0.111	-0.537	0.418	0.960	0.211	0.247	-0.118	-0.301	-0.496	-0.177	0.013
<b>Alox</b>	0.967	-0.996	0.830	-0.087	-0.557	0.440	0.967	0.235	0.270	-0.094	-0.278	-0.475	-0.154	-0.102
<b>Fep</b>	0.963	-0.994	0.821	-0.102	-0.554	0.426	0.963	0.220	0.255	-0.109	-0.292	-0.489	-0.169	0.004
<b>Alp</b>	0.940	-0.983	0.776	-0.176	-0.480	0.357	0.940	0.146	0.183	-0.183	-0.363	-0.552	-0.242	-0.079
<b>TS</b>	0.910	-0.965	0.724	-0.254	-0.409	0.282	0.910	0.067	0.103	-0.261	-0.436	-0.617	-0.319	0.158
<b>Or.S</b>	0.869	-0.938	0.659	-0.340	-0.325	0.194	0.869	-0.023	0.014	-0.347	-0.515	-0.686	-0.403	0.246
<b>In.S</b>	0.996	-0.997*	0.913	0.084	-0.691	0.587	0.996	0.398	0.431	0.078	-0.109	-0.318	0.017	-0.182

\* = Correlation is significant at the 0.05 level, Or.C= Organic carbon, Or.S= Organic sulphur, In.S=Inorganic sulphur, All the parameters in row are kinetic model rate constants (see pages 30 and 36)

#### 4.6.2 Soil from Basement Complex rock

Sulphate desorption parameters were affected by some soil properties (Table 4.10). Organic S correlated positively with second- order constants ( $k_2$ ) (0.999\*) and ( $q_e$ ) (0.999\*). Organic S also correlated positively and significantly with Elovich constant ( $\beta$ ) (0.999\*), and negatively correlated with Elovich constant ( $\alpha$ ) (-0.998\*) and parabolic diffusion constant ( $R$ ) ( $r = -0.999^*$ ). The effective behaviour of organic matter on the sorption of anions such as sulphate could either augment or reduce the S adsorption in soils. This positive correlation indicates that S desorption increases with increasing soil organic matter which has been attributed to reduction of the positive potential through formation of organo- metal complex compound (a strong precipitate of Al or Fe with organic matter) , thus causing a promotion in the repulsion of the S and subsequent higher desorption. First order constant ( $q_0$ ) correlated negatively with pyrophosphate extractable Fe<sub>p</sub> (-1.000\*). This is expected because the retention of S in soils is sometimes due to binding by sesquioxides, thus increasing S adsorption in soils and subsequent lower S desorption. Langmuir constant ( $k_L$ ) was highly correlated with silt (1.000\*\*). This implies that Langmuir modeling is directly related to silt content. Silt correlated positively and significantly with Freundlich constant ( $n_f$ ) (1.000\*), but negatively correlated with Freundlich constant ( $k_f$ ) (-0.997\*). Freundlich constants ( $n_f$ ) and ( $k_f$ ) of S desorption data have direct or inverse relationships with silt content, respectively.

**Table 4.10: Correlation between kinetic parameters and soil properties of soils derived from Basement complex rock (BCR)**

	<b>k<sub>1</sub></b>	<b>q<sub>0</sub></b>	<b>k<sub>2</sub></b>	<b>q<sub>e</sub></b>	<b>B</b>	<b>a</b>	<b>n<sub>fp</sub></b>	<b>k<sub>fp</sub></b>	<b>R</b>	<b>b</b>	<b>q<sub>max</sub></b>	<b>k<sub>L</sub></b>	<b>n<sub>f</sub></b>	<b>k<sub>f</sub></b>
<b>Sand</b>	-0.855	-0.047	-0.856	-0.857	-0.907	0.899	0.925	0.844	0.892	0.482	-0.918	-0.972	-0.962	0.984
<b>Silt</b>	0.957	-0.202	0.957	0.958	0.983	-0.979	-0.990	-0.951	-0.976	-0.684	0.988	1.000**	1.000*	-0.997*
<b>Clay</b>	0.433	0.586	0.434	0.436	0.530	0.512	-0.567	-0.413	-0.499	0.076	0.552	0.685	0.655	-0.728
<b>pH</b>	-0.033	0.894	-0.032	-0.030	0.078	-0.057	-0.122	0.055	-0.042	0.528	0.104	0.272	0.231	-0.329
<b>Or.C</b>	0.529	0.494	0.529	0.531	0.619	-0.603	-0.653	-0.510	-0.591	-0.033	0.640	0.761	0.733	-0.798
<b>Ca</b>	0.599	0.418	0.600	0.601	0.684	-0.669	-0.716	-0.581	-0.657	-0.119	0.703	0.814	0.789	-0.847
<b>Mg</b>	0.828	0.099	0.828	0.829	0.885	-0.875	-0.905	-0.815	-0.867	-0.436	0.897	0.959	0.946	-0.974
<b>K</b>	0.866	0.027	0.866	0.869	0.916	-0.908	-0.933	-0.855	-0.901	-0.500	0.926	0.977	0.967	-0.988
<b>Na</b>	-0.189	-0.773	-0.190	-0.192	-0.296	0.277	0.338	0.167	0.262	-0.327	-0.321	-0.478	-0.441	0.529
<b>CEC</b>	-0.861	-0.038	-0.861	-0.862	-0.912	0.903	0.929	0.849	0.896	0.491	-0.922	-0.974	-0.964	0.986
<b>BS</b>	0.774	0.187	0.775	0.776	0.839	-0.828	-0.863	-0.760	-0.819	-0.354	0.854	0.930	0.913	-0.950
<b>Fed</b>	-0.807	-0.135	-0.807	-0.808	-0.867	0.857	0.888	0.794	0.849	0.403	-0.880	-0.948	-0.934	0.965
<b>Ald</b>	-0.947	0.734	-0.947	-0.946	-0.905	0.914	0.886	0.954	0.920	0.981	-0.894	-0.805	-0.829	0.768
<b>Feox</b>	-0.772	-0.191	-0.772	-0.774	-0.837	0.826	0.861	0.758	0.817	0.351	-0.852	-0.928	-0.912	0.949
<b>Alox</b>	-0.860	-0.039	-0.860	-0.861	-0.911	0.902	0.928	0.848	0.896	0.489	0.922	-0.974	-0.964	0.986
<b>Fep</b>	0.492	-1.000*	0.491	0.489	0.393	-0.412	-0.352	-0.511	-0.425	-0.861	0.368	0.205	0.246	-0.146
<b>Alp</b>	0.281	-0.978	0.281	0.278	0.173	-0.194	-0.130	-0.302	-0.209	-0.723	0.147	-0.023	0.019	0.082
<b>TS</b>	0.552	-0.996	0.551	0.549	0.456	-0.474	-0.416	-0.570	-0.488	-0.895	0.432	0.273	0.313	-0.215
<b>Or.S</b>	0.999*	-0.445	0.999*	0.999*	0.997*	-0.999*	-0.993	-0.998*	-0.999*	-0.847	0.995	0.963	0.974	-0.946
<b>In.S</b>	-0.189	-0.773	-0.190	-0.192	-0.296	0.227	0.338	0.167	0.262	-0.327	-0.321	-0.478	-0.441	0.529

\*\* = Correlation is significant at the 0.01 level, \* =Correlation is significant at the 0.05 level, Or.C= Organic carbon, Or.S= Organic sulphur, In.S=Inorganic sulphur, All the parameters in row are kinetic model rate constants (see pages 30 and 36)

### 4.6.3 Kerri-Kerri Formation

Significant correlation between kinetic parameters and soil properties is presented in Table 4.11. A significant and negative correlation of first-order constant ( $k_1$ ) was obtained with TS (-0.998\*). Fractional power constant ( $k_{fp}$ ) correlated negatively and significantly with sand (-0.999\*), but positively with silt (0.999\*). Fractional power ( $n_{fp}$ ) also correlated negatively and significantly with Org.S (-0.999\*). Parabolic diffusion constant (R) also correlated negatively and positively with sand (-0.999\*), but positively with silt (0.999\*). Langmuir constant ( $q_{max}$ ) correlated positively and significantly with organic carbon (1.000\*). Several workers have reported significant correlation between Langmuir constant ( $q_{max}$ ) and organic carbon (Murthy, 2004; Alves and Lavorenti, 2004; Pigna *et al.*, 2007; Uzoho *et al.*, 2014; Maida and Nalivata, 2016) all for sulphate sorption data in soils. This implied that increases of organic matter could increase the level of S desorption of adsorbed S from sorptive sites. In addition, competitive sorption of organic matter can increase the solubility of adsorbed sulphate and release into soil solution (Sokolova and Alekseeva, 2008).

A significant and positive correlation of Alox content was observed with Langmuir constant ( $q_{max}$ ) (1.000\*) and Langmuir constant ( $k_L$ ) (0.998). This implies that desorption of S is directly related to oxalate extractable Al. Na correlated positively and significantly with Freundlich constant ( $k_f$ ) (1.000\*), but negatively correlated with Freundlich constant ( $n_f$ ) (-0.999\*). Correlation results indicated that organic matter had a strong influence on predict the fate and availability of S in all studied soils.

**Table 4.11: Correlation between kinetic parameters and soil properties of soils derived from Kerri-Kerri formation (KKF)**

	<b>k<sub>1</sub></b>	<b>q<sub>0</sub></b>	<b>k<sub>2</sub></b>	<b>Q<sub>e</sub></b>	<b>B</b>	<b>a</b>	<b>n<sub>fp</sub></b>	<b>k<sub>fp</sub></b>	<b>R</b>	<b>b</b>	<b>q<sub>max</sub></b>	<b>k<sub>L</sub></b>	<b>n<sub>f</sub></b>	<b>k<sub>f</sub></b>
<b>Sand</b>	-0.986	-0.937	-0.973	-0.987	0.995	-0.992	-0.996	-0.999*	-0.999*	-0.939	0.823	0.773	0.732	-0.717
<b>Silt</b>	0.986	0.937	0.973	0.987	-0.995	0.992	0.996	0.999*	0.999*	0.939	-0.823	-0.773	-0.732	0.717
<b>Clay</b>	0.979	0.743	0.819	0.859	-0.888	0.876	0.958	0.912	0.914	0.748	-0.974	-0.952	-0.931	0.923
<b>pH</b>	-0.589	-0.103	-0.223	-0.294	0.351	-0.326	-0.519	-0.401	-0.406	-0.110	0.874	0.911	0.935	-0.943
<b>Or.C</b>	-0.908	-0.575	-0.670	-0.722	0.763	-0.746	-0.869	-0.797	-0.800	-0.580	1.000*	0.996	0.989	-0.986
<b>Ca</b>	-0.648	-0.943	-0.895	-0.861	0.828	-0.842	-0.710	-0.796	-0.794	-0.941	0.267	0.187	0.124	-0.102
<b>Mg</b>	-0.618	-0.930	-0.878	-0.841	0.806	-0.821	-0.683	-0.773	-0.770	-0.927	0.230	0.149	0.087	-0.065
<b>K</b>	-0.583	-0.912	-0.856	-0.861	0.779	-0.795	-0.649	-0.744	-0.741	-0.909	0.187	0.105	0.042	-0.020
<b>Na</b>	0.813	0.410	0.517	0.578	-0.627	0.606	0.760	0.668	0.672	0.416	-0.982	-0.994	-0.999*	1.000*
<b>CEC</b>	-0.534	-0.887	-0.824	-0.781	0.741	-0.759	-0.604	-0.704	-0.700	-0.884	0.129	0.047	-0.016	0.038
<b>BS</b>	0.252	-0.269	-0.150	-0.078	0.017	-0.043	0.169	0.037	0.042	-0.262	-0.635	-0.697	-0.741	0.755
<b>Fed</b>	-0.696	-0.962	-0.922	-0.892	0.863	-0.876	-0.754	-0.834	-0.831	-0.961	0.329	0.250	0.188	-0.167
<b>Ald</b>	0.802	0.994	0.972	0.953	-0.932	0.942	0.849	0.912	0.910	0.993	-0.476	-0.402	-0.343	0.323
<b>Feox</b>	0.793	0.992	0.969	0.949	-0.927	0.937	0.842	0.906	0.904	0.991	-0.464	-0.389	-0.331	0.310
<b>Alox</b>	-0.896	-0.551	-0.648	-0.702	0.744	-0.726	-0.855	-0.779	-0.782	-0.557	1.000*	0.998*	0.993	-0.990
<b>Fep</b>	0.247	0.700	0.608	0.549	-0.497	0.520	0.328	0.450	0.445	0.695	0.184	0.264	0.324	-0.345
<b>Alp</b>	0.778	0.988	0.963	0.940	-0.918	0.928	0.829	0.895	0.893	0.987	-0.442	-0.366	-0.307	0.286
<b>TS</b>	-0.998*	-0.834	0.895	-0.925	0.946	-0.937	-0.990	-0.962	-0.964	-0.874	0.930	0.897	0.867	-0.856
<b>Or.S</b>	-0.993	-0.917	-0.959	-0.977	0.988	-0.984	-0.999*	-0.995	-0.995	-0.920	0.852	0.806	0.767	-0.753
<b>In.S</b>	-0.739	-0.300	-0.414	-0.479	0.531	-0.509	-0.679	-0.576	-0.580	-0.307	0.954	0.975	0.987	-0.991

\*\* = Correlation is significant at the 0.01 level, \* = Correlation is significant at the 0.05 level, Or.C= Organic carbon, Or.S= Organic sulphur, In.S=Inorganic sulphur, All the parameters in row are kinetic model rate constants (see pages 30 and 36)



#### **4.7 Effect of Biochar on Kinetics Desorption of Sulphate**

Comparative studies of soils without biochar and soils with biochar from soil of different parent materials were carried out to determine the effect of biochar on kinetics desorption of sulphate at different time intervals. The mean concentration of sulphate desorbed by soils without biochar and soils with biochar at different time intervals were not significantly different ( $p > 0.05$ ) (Table 4.12). This implies that the influence of this type of biochar in all the studied soils across the three different parent materials were negligible. However, a minor effect of biochar application on increased desorption of adsorbed sulphate was observed. A similar observation was made by Uchimiya *et al.* (2010) and Borchard *et al.* (2012). Sokolova and Alekseeva (2008) reported that a consequence of the pronounced increase in pH related with application of biochar might be reasoned for increase in amount of sulphate desorbed. This situation might also be true for the increase amount of sulphate desorbed in all the soils in the current study. In addition to pH, competitive sorption of biochar can increase the solubility of amount of adsorbed sulphate (Sokolova and Alekseeva, 2008; Borchard *et al.*, 2012).

It was observed that the concentration of sulphate adsorbed slightly decreased with the presence of this type of biochar (Appendix 4). Application of BC in soils might raise soil pH which may be reason for the slight decreased in S adsorption (Borchard *et al.*, 2012; Yao *et al.*, 2012). For this study, the application of biochar into soil could not justify its cost of production. Under current situation farmers will rarely adopt biochar incorporation into soils due to its small effects and difficulty in sourcing the materials that is large enough for farm application.

**Table 4.12: Effect of biochar on kinetics desorption of sulphate at different time intervals**

Time (minutes)	Soil without biochar	mg/kg	Soil with biochar	LOS
30	31.25		31.47	NS
60	30.77		31.02	NS
150	27.51		27.41	NS
180	27.00		27.16	NS
240	23.12		23.23	NS
Total	27.93		28.06	NS

Mean values in row are not significantly different from one another at 5% NS= Not significant, LOS= Level of Significance

## CHAPTER FIVE

### 5.0 Summary, Conclusion and Recommendations

#### 5.1 Summary

The physical and chemical properties of soils developed over three parent material, namely; Chad formation (CF), Basement complex rock (BCR) and Kerri-Kerri formation (KKF) show that the soil textures characterized by higher clay contents in the sub-soils than in the surface soils. Sand dominated the particles size fractions in all the studied soils (Table 4.1). Soil pH in water fell within slightly acidic to neutral. The mean values of soil pH in water and CaCl<sub>2</sub> were significantly ( $p > 0.05$ ) different by soil parent materials (Table 4.2). Such fundamental differences in these parent materials account for the variation in pH. The soils are low in organic carbon (Table 4.3), irrespective of soil parent materials. The exchangeable Ca<sup>2+</sup> and Na<sup>+</sup> were rated low to moderate while Mg<sup>2+</sup> and K<sup>+</sup> rated moderate by soil parent materials. However, surface soils values for all exchangeable bases and CEC higher than their corresponding sub-surface soils, irrespective of parent materials. The significant influence of parent material on forms, content and distribution of Fe and Al oxides was noted in these soils. The trend in magnitude by various forms of oxides and parent materials are as follows: Dithionite > Oxalate > Pyrophosphate and BCR > KKF > CF, respectively (Table 4.5). However, values of forms of Fe and Al oxides were higher in sub-surface soils compared to their surface soils across the three parent materials and also the concentration of the various forms Al oxides are lower than that of Fe oxides. It was observed that the extraction procedure for Fe also releases Al, so that levels of Fe might be overestimated or probably due to abundance of ferromagnesian minerals in Nigerian savanna. All forms of sulphur in this study were found to be low and followed the order by parent materials as follows: CF  $\geq$  KKF  $\geq$  BCR (Table 4.5).

Desorption of adsorbed S is time-dependent in soils and the results showed that the rate of desorption of adsorbed S from the soils decreased with increasing shaking time in all the studied soils. Initially, desorption was rapid with > 65% being desorbed in 30 minutes which considered as good contact time for describing S desorption maximum and then slowed down up to 240 minutes (Figure 4.1) in all soils developed over three different parent materials.

A variety of kinetic models were tested to compare the best fitted models to describe S desorption data. It was found that parabolic diffusion and first-order satisfactorily described S desorption as shown by their relatively high  $R^2$  values and lowest S.E values in all soil parent materials (Figure 4.2).

The modeling of sulphate is critical in predicting the fate of added S, mobility and making proper S fertilizer recommendation to ensure significant farm productivity. The results revealed that both isotherm equations (Langmuir and Freundlich) were suitable in describing S desorption data as judged by  $R^2$  value which is greater than 0.98 in all the soils from different parent materials. However, in view of the lower SE, Langmuir equation gave a better fit to the experimental data in this study (Table 4.8). The goodness of fit of this equation reflects monolayer desorption which is an indication of rapid desorption of labile form of S from external sites into the soil solution.

The study results revealed that Freundlich modeling of S desorption data is directly and significantly related to soil pH while Langmuir modeling correlated positively with OC in the CF soils, OC correlated positively and significantly with Elovich constant ( $\beta$ ) (0.999\*) in the BCR soils, and Langmuir modeling of S desorption data is directly related to OC and Alox in the KKF soils. The positive and significant correlation of OC with S desorption parameters may probably

be due to dissolution of Fe and Al oxides leading to destruction of sorptive sites as organic matter decomposes.

The results also revealed that the biochar used in this study did not have any significant effect on release of adsorb S (Table 4.12). However, the type of BC tested in this study had a very little S sorption and desorption property. Several researchers had reported biochars had a little or no effect on anions adsorption and desorption processes in soils.

## **5.2 Conclusion**

Rates of desorption in this study was biphasic and also hysteresis in nature. Increase of shaking time caused abrasion of soil particles leading to the disintegration of soil aggregates and consequent exposure of new surface sites and greater sorption, thus lowering the rate of sulphate desorption. A shaking time at 150 was enough for the system to reach equilibrium and at 30 minutes was considered to be a good contact time for sulphate desorption maximum in all the studied soils. Conformity of S desorption data to first- order equation is an indication of a probable ligand exchange of sulphate ion during the desorption process and to parabolic diffusion equation suggested that diffusion-controlled phenomena are rate- limiting steps.

Soil pH, organic carbon and forms of iron and aluminium oxides are critically clearly important parameters for regulating rate of sulphate desorption in soils. The ability of biochar to adsorb and desorb anions is not universal depends on type of feedstock and plant nutrients. Therefore, the findings of this dissertation are pivotal for understanding the release, bioavailability and mobility of added S fertilizers in soils, and to make proper S fertilizer recommendations to ensure sustainable and profitable crop production and environmental protection.

### **5.3 Recommendations**

The formulation of the added S ion should be predicted and modeled not only on rapid desorption at 30 minutes but also at extended time up to 240 minutes. It is recommended that sulphur management practice in the farm should be tied up with OM management. Since, OM acts as a source, retainer and releaser of soil sulphate. It is also recommended that affinity of BC to release plant nutrients should be tested before applying to soils as amendment. It is also recommended to conduct plant growth studies to see whether this type of BC have significant effect on crop performance or not.

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## APPENDICES

### Appendix 1: Amount of sulphate desorbed at different time intervals

Sampling Location	Depth (cm)	Adsorbed S 24 hours	Release of adsorbed sulphate at different time interval (mg / kg)				
			30minutes	60minutes	150minutes	180minutes	240minutes
<b>CHAD FORMATION (CF)</b>							
Digiza	0-15	42.17	32.39	31.88	29.68	29.45	25.27
Digiza	15-30	41.15	32.30	31.57	29.22	28.74	24.82
Gongo	0-15	42.34	31.06	30.53	29.11	29.00	24.82
Gongo	15-30	42.52	30.04	29.62	26.85	26.68	23.41
Guda	0-15	39.65	34.96	34.25	31.35	31.29	28.74
Guda	15-30	41.06	33.49	32.72	30.15	29.87	26.53
<b>BASEMENT COMPLEX ROCK (BCR)</b>							
Tawayla	0-15	42.21	31.53	31.13	28.62	28.51	24.49
Tawayla	15-30	43.03	30.10	29.41	26.58	26.51	22.80
Jaberi	0-15	42.94	30.75	30.00	27.20	27.13	22.30
Jaberi	15-30	43.38	30.16	29.84	25.63	25.06	21.48
Zenabari	0-15	42.48	32.08	31.77	28.81	28.72	23.31
Zenabari	15-30	43.23	29.96	29.19	26.41	26.31	20.63
<b>KERRI – KERRI FORMATION (KKF)</b>							
Kauyan Jalo	0-15	42.18	30.49	30.07	25.16	25.08	22.52
Kauyan Jalo	15-30	41.28	30.16	29.80	24.56	24.11	22.67
Doguwa	0-15	41.85	31.92	31.74	25.80	25.77	22.20
Doguwa	15-30	41.85	30.23	29.83	24.93	24.30	20.53
Kwari	0-15	42.03	31.88	31.89	26.52	26.02	20.57
Kwari	15-30	43.71	28.94	28.54	23.54	23.40	19.09

## Appendix 2: Percentage of sulphate desorbed at different time intervals

Sampling Location	Depth (cm)	Percentage of adsorb S 24 hours	Percentage of desorb sulphate at different time interval (mg/kg)				
			30minutes	60minutes	150minutes	180minutes	240minutes
<b>CHAD FORMATION (CF)</b>							
Digiza	0-15	84.34	76.81	75.60	70.38	69.84	59.92
Digiza	15-30	82.30	78.49	76.72	71.01	69.84	60.32
Gongo	0-15	84.68	73.36	72.11	68.75	68.49	58.62
Gongo	15-30	85.04	70.65	69.66	63.15	62.75	55.06
Guda	0-15	79.30	88.17	86.38	79.07	78.92	72.48
Guda	15-30	82.12	81.56	79.69	73.43	72.75	64.61
<b>BASEMENT COMPLEX ROCK (BCR)</b>							
Tawayla	0-15	84.42	74.70	73.75	67.80	67.54	58.02
Tawayla	15-30	86.06	69.95	68.35	61.77	61.61	52.99
Jaberi	0-15	85.88	71.61	69.86	63.34	63.18	51.93
Jaberi	15-30	86.76	69.53	68.79	59.08	57.77	49.52
Zenabari	0-15	84.96	75.52	74.79	67.82	67.61	54.87
Zenabari	15-30	86.46	69.30	67.52	61.09	60.86	47.72
<b>KERRI – KERRI FORMATION (KKF)</b>							
Kauyan Jalo	0-15	84.36	72.29	71.29	59.65	59.46	53.39
Kauyan Jalo	15-30	82.56	73.06	72.19	59.50	58.41	54.92
Doguwa	0-15	83.70	76.27	75.84	61.65	61.58	53.05
Doguwa	15-30	83.70	72.23	71.28	71.52	58.06	49.06
Kwari	0-15	84.06	75.85	75.87	63.10	61.91	48.94
Kwari	15-30	87.42	66.21	65.29	53.85	53.53	43.67



**Table 4.3: Amount of sulphate desorbed from soils with biochar at different time intervals**

Sampling Location	Depth (cm)	Adsorbed S 24 hours	Release of adsorbed sulphate at different time interval (mg / kg)				
			30minutes	60minutes	150minutes	180minutes	240minutes
<b>CHAD FORMATION (CF)</b>							
Digiza	0-15	41.44	32.64	31.98	29.88	29.71	25.34
Digiza	15-30	40.44	32.47	31.81	29.37	28.84	24.35
Gongo	0-15	41.64	31.36	30.83	29.41	29.15	24.95
Gongo	15-30	41.87	30.34	29.89	27.05	26.84	23.46
Guda	0-15	38.91	35.17	34.53	31.60	31.45	28.85
Guda	15-30	40.26	33.74	32.98	30.30	30.04	26.62
<b>BASEMENT COMPLEX ROCK (BCR)</b>							
Tawayla	0-15	41.76	31.77	31.30	28.80	28.62	24.59
Tawayla	15-30	42.63	30.29	29.56	26.75	26.61	22.89
Jaberi	0-15	42.33	31.00	30.26	27.40	27.24	22.47
Jaberi	15-30	43.01	30.38	30.00	25.75	25.14	21.58
Zenabari	0-15	42.11	32.21	32.04	29.05	28.83	23.49
Zenabari	15-30	42.98	30.11	29.53	26.68	26.61	20.81
<b>KERRI – KERRI FORMATION (KKF)</b>							
Kauyan Jalo	0-15	41.37	30.66	30.26	25.38	25.21	22.71
Kauyan Jalo	15-30	40.72	30.38	30.07	24.77	24.32	22.90
Doguwa	0-15	41.24	32.17	32.01	25.98	25.90	22.38
Doguwa	15-30	41.16	30.44	30.16	25.10	24.53	20.73
Kwari	0-15	41.28	32.07	32.03	26.61	26.12	20.72
Kwari	15-30	43.04	29.17	29.08	23.56	23.75	19.28

**Appendix 4: % of sulphate desorbed from soils mixed with biochar at different time intervals**

Sampling Location	Depth (cm)	Percentage of adsorb S	Percentage of desorb sulphate at different time interval (mg / kg)				
			24 hours	30minutes	60minutes	150minutes	180minutes
<b>CHAD FORMATION (CF)</b>							
Digiza	0-15	82.88	78.76	77.17	72.10	71.69	61.15
Digiza	15-30	80.88	80.29	78.66	72.63	71.32	60.21
Gongo	0-15	83.28	75.31	74.04	70.63	70.00	59.92
Gongo	15-30	83.74	72.46	71.39	64.60	64.10	56.03
Guda	0-15	77.82	90.39	88.74	81.21	80.83	74.15
Guda	15-30	80.52	83.81	81.92	75.26	74.62	66.12
<b>BASEMENT COMPLEX ROCK (BCR)</b>							
Tawayla	0-15	83.52	76.08	74.95	68.97	68.53	58.88
Tawayla	15-30	85.26	71.05	69.34	62.75	62.42	53.69
Jaberi	0-15	84.66	73.23	71.49	64.73	64.36	53.08
Jaberi	15-30	86.02	70.63	69.75	59.87	58.45	50.17
Zenabari	0-15	84.22	76.49	76.09	68.99	68.46	55.78
Zenabari	15-30	85.96	70.06	68.71	62.08	61.91	48.42
<b>KERRI – KERRI FORMATION (KKF)</b>							
Kauyan Jalo	0-15	82.74	74.11	73.14	61.35	60.94	54.89
Kauyan Jalo	15-30	81.44	74.61	73.85	60.83	59.72	56.24
Doguwa	0-15	82.48	78.01	77.62	63.00	62.80	54.28
Doguwa	15-30	82.32	73.96	73.28	60.98	59.60	50.36
Kwari	0-15	82.56	77.69	77.59	64.46	63.28	50.19
Kwari	15-30	86.08	67.77	67.57	54.74	55.18	44.80