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LABORATORY OF PHYSICAL AND ANALYTICAL APPLIED CHEMISTRY
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Production and amendment of biochar from coffee husk and cocoa pod husk on an acid soil from West Cameroon: Effects on soil chemical properties and phosphorus sorption/desorption

A Thesis submitted in partial fulfillment of the requirements for the award of a
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ATTESTATTION DE CORRECTION DE LA THESE DE DOCTORAT/Ph.D DE M. POUANGAM NGALANI Gilles

Nous soussignés **DJOUFAC WOUMFO Emmanuel**, Professeur, Président du jury; **NGAMENI Emmanuel**, Professeur, Rapporteur et **NANSEU NJIKI Charles Péguy**, Professeur, Examinateur, **TCHAKOUTE KOUAMO Hervé**, Maître de conférences, Examinateur ; attestons que **M. POUANGAM NGALANI Gilles**, Matricule **06T370**, a bel et bien effectué toutes les corrections qui lui ont été exigées par les membres du jury lors de sa soutenance du **15 Janvier 2024** dans la salle S01/02 de la Faculté des Sciences de l'Université de Yaoundé I, sur le sujet intitulé « **Production and amendement of biochar from coffee husk and cocoa pods husk on an acid soil from West Cameroon : Effects on soil chemical properties and phosphorus sorption/desorption** » en vue de l'obtention du Diplôme de Doctorat/Ph.D en Chimie Inorganique option Chimie Analytique.

En foi de quoi la présente attestation lui est délivrée pour servir et valoir ce que de droit.

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TCHAKOUTE KOUAMO Hervé,
Maître de Cconférences

DEDICATION

To

My daughters ***Dalia POUANGAM and Kendra POUANGAM***

And to

My parents ***Mr. and Mrs. POUAGAM***

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LIST OF ABBREVIATIONS

SOC: Soil organic carbon

EC: Electrical conductivity

PZC: Point of zero charge

CH350: Biochar produced from coffee husk at 350 °C

CH550: Biochar produced from coffee husk at 550 °C

CP350: Biochar produced from cocoa pod husk at 350 °C

CP550: Biochar produced from cocoa pod husk at 550 °C

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ABSTRACT

Soils in West Cameroon are acidic and have a low level of available phosphorus (P) which leads to a decline in plant growth and crop yield. With the increase in demand for food, biochar has been the focus of much attention as a soil amender for soil improvement. The main objective of this work is to evaluate the liming and fertility properties of biochar, together with it effect on the chemical properties of soils, coupled with the consequences for phosphorus sorption and desorption. In this study, acid soils sampled in Bafang were amended with biochar produced from coffee husk and cocoa pod husk at two different temperatures (350 and 550 °C). The soils were amended at different rates (0, 20, 40, and 80 g/kg) and different incubation days (7, 14, 30, 45, and 60 days). Selected soil properties such as pH, electrical conductivity (EC), exchangeable acidity, exchangeable aluminium, exchangeable iron, available P, and soil organic carbon (SOC) were examined under the effect of biochar amendments. Sorption experiments and data were fitted into the Langmuir and Freundlich isotherm models in order to evaluate soil P sorption capacity and its affinity to soil amended with biochar. Moreover, desorption studies were done to evaluate the availability of P in soil amended with biochar after sorption. The results showed that biochar amendments significantly improved soil pH and soil electrical conductivity compare to the to control. Furthermore, biochar improved the available P in acid soil, though readsorption occurred with increasing incubation time. A significant increase in SOC was observed as compared to the control. The point of zero charge (PZC) of biochar amended soil was higher than the control and increased with amendment rate. The soil-biochar mixture resulted in a decrease in the sorption capacity as compared to the control, and the decrease was predominant with a rising amendment rate. Furthermore, the desorption of P from the soil-biochar mixture was enhanced with biochar added at a higher rate and produced at a higher temperature. Biochar plays the dual role of a liming agent and a source of P fertilizer nutrients. Moreover, biochar addition to acid soils reduces P fixation and improves P desorption in soil solutions, thereby providing more available P in the soil solution and better conditions for plant growth.

Keywords: Biochar; acid soil; soil pH, available P; exchangeable Al, Phosphorus, sorption

RESUME

Les sols de l'Ouest Cameroun sont acides et ont une faible teneur en phosphore (P) disponible, ce qui entraîne un déclin de la croissance des plantes et du rendement des cultures. Avec l'augmentation de la demande alimentaire, le biochar fait l'objet d'une attention particuliere en tant qu'amendement. La présente recherche a pour objectf général l'évaluation des propriétés de chaulage et la fertilité du biochar, ainsi que son effet sur les propriétés chimiques du sol acide et les conséquences sur la sorption/désorption du P. Dans cette étude, les sols acides échantillonnés à Bafang ont été amendés avec du biochar produit à partir des pulpes de café et des coques de cacao à deux températures différentes (350 et 550 °C). Les sols ont été amendés à diffèrent taux de biochar (0, 20, 40 et 80 g/kg) et à différents nombres de jours d'incubation (7, 14, 30, 45 et 60 jours). Certaines propriétés du sol, comme le pH, la conductivité électrique (CE), l'acidité échangeable, l'aluminium échangeable, le fer échangeable, le P disponible et le carbone organique du sol (SOC) ont été examinées sous l'effet des amendements des biochars. Les données obtenues des expériences de sorption ont été intégrées aux modèles d'isothermes de Langmuir et de Freundlich avec pour but d'évaluer la capacité de sorption du P et son affinité avec le sol amendé avec du biochar. Des études de désorption ont également été menées pour évaluer la disponibilité du P dans le sol amendé avec du biochar après la sorption. Les résultats obtenus ont montré que les amendements du biochar ont amélioré considérablement le pH, la CE. De plus le biochar a augmenté le P disponible, même si, la réadsorption s'est produite avec une période d'incubation plus longue. Une augmentation significative du SOC a été observée comparativement au sol témoin. Le point de charge nul du sol amendé était plus élevé que celui du sol témoin et augmentait avec le taux d'amendement. Le mélange sol-biochar a provoqué une diminution de la capacité de sorption par rapport au témoin et la diminution a été prédominante avec l'augmentation du taux d'amendement. En outre, la désorption du P du mélange sol-biochar a été améliorée par l'addition de biochar à un taux plus élevé et produite à haute température. Ce travail a montré que le biochar joue le double rôle de matériau de chaulage et de source d'engrais à base de P. De plus, l'ajout du biochar aux sols acides réduit la fixation du P au sol et améliore la désorption du P à la solution du sol, offrant ainsi plus de P disponible dans la solution du sol et de meilleures conditions pour la croissance des plantes.

Mots clés : Biochar; sol acide; pH du sol, P disponible; Al échangeable, Phosphores, sorption.

GENERAL INTRODUCTION

This section will discuss the general background of this research, the objectives and the thesis outline

General background of this research

Soil acidity and phosphorus deficiency have been recognized as two of the main factors restraining plant growth and yield in acid soils. Acid soils in Africa are widely spread in the tropics [1] and in Cameroon, they exist in some areas in the Western region [2]. The presence of acid soils occurs with a predominance in H^+, Al^{3+} in the soil solution [3], which inhibits both cell elongation and cell division, resulting in a reduction in root elongation in many plants and also interferes with the uptake, transport, and use of several essential elements [4]. It also leads to a high level of P fixation via reaction with (oxyhydr)oxides of Al and Fe found in clay minerals and thus deprives plant of P resulting in poor growth [5,6]. The fixation of P in soils is influenced by soil organic matter, soil pH, soil exchangeable Al, Fe, amount and type of silicate clays, and calcium carbonate content [7,8] which affect their biogeochemical processes (dissolution, adsorption, and, precipitation). Coupled with soil acidity in the tropics, sustainable agriculture is facing the constraint of low soil organic matter content due to accelerated mineralization [9], erosion, leaching [10], also inappropriate cultivation practices.

With the current increase in food demands, potential input resources and management practices are put in place with more or less favourable results. One of the ways to remediate these limitations is the amendments technique, which includes the application of lime [11], the addition of green manures [12], compost [13], wood ash [14], direct P fertilization [15], rock phosphate [16]. The above approach has its limitations, among them:

(i) economy (purchase and application of large quantities of lime and P fertilizers);
(ii) overliming precipitates P ions with Ca and can also lead to soil compaction [17];
(iii) direct application of manure and excess P may pose a risk of surface and groundwater impairment [18];
(iv) poor stability of organic matter due to high amount of labile C in crop residue or compost [19].

An alternative to these different limitations is the use of biochar, which gives the possibility to bring down several birds with the same stone, creating a lot of hope. Biochar has received great attention as an alternative option to overcome soil limitations. This is a material derived from the pyrolysis of biomass in an atmosphere containing little or no oxygen [20]. Commonly used biomasses are agricultural and forestry residues, animal wastes, food processing waste, paper waste, municipal solid waste, and sludge [21] which is abundant and of low cost. Coffee and cocoa are two of the main cash crops grown in Cameroon. Waste produced from these crops, when poorly disposed of, can generate serious environmental problems. In Bafang, coffee husk is disposed of, in the river, which can cause siltation of rivers [22], and poor disposal of cocoa pods in cocoa farms can be a source of black pod rot for cocoa plants [23]. Thus there is a need to properly manage these biomasses to protect the environment.

Biochar application to acid soils alters the soil physicochemical properties [24] and improves P availability [25]. Biochar addition ameliorates soil acidity by reducing the quantity of H^+, Al^{3+}, and $Fe^{3+,2+}$ due to its alkaline nature and thus reducing P precipitation [26]. Also, biochar consists of condensed aromatic forms of organic carbon, which are recalcitrant and do not decompose easily in soils [27], preventing C from returning to the atmosphere as CO_2 within a short period. Earlier studies have reported that biochar produced from different feedstocks and pyrolysis temperatures has diverse physical and chemical properties such as functional groups, mineral contents, pH, $CaCO_3$ content, cation exchange capacity, and surface area [28].

The study of changes in soil chemical properties due to the application of biochar is still a current research, in order to better understand the mechanisms sustaining these changes. Moreover, biochar amended in acid soils has contradicting results on the fixation of P through sorption studies. Some works have presented an increase in sorption of P compared to the control acid soils due to the binding of phosphate to the carbonates and oxides of Ca and Mg [29,30] while on the contrary, low sorption of P was also observed in the control acid soils and was attributed to the precipitation of Al^{3+} and Fe^{3+} [31] and the repulsion of the negative phosphate ions by the negative charges [32,33].

The government of Cameroon, during COP 26 became the first country to integrate biochar production into its climate change strategy [34]. The Cameroonian delegation informed environmental experts at COP 26 in Glasgow that by 2030, about fifty biochar production plants will be operational, and to attain these objectives, the government of Cameroon has engaged the services of the company Netzero. Thus, any research work on the possibility of producing biochar from feedstocks pyrolyzed at different temperatures and applied to acid soils should be considered and explored in terms of changes in the soil chemical properties with the effect on the sorption and desorption abilities of the amended soil.

Research objectives

Main objective

The aim of this study is to investigate the possibility of using biochar as a soil amendment technique to ameliorate the condition of the acid soil. Specifically, it intends to evaluate the effect of biochar derived from coffee husk and cocoa pods on the chemical properties of acid soils and the effect of biochar amended acid soil on P sorption and desorption.

Specific objectives (with sub-objectives)

In order to achieve the main objective, three sub-objectives have been defined, namely:

Sub-objective 1: To sample the acid soil and the biomass (coffee husk and cocoa pod husk) in Bafang, West region of Cameroon, and produce the biochar at two different temperatures followed by characterization.

Sub-objective 2: To evaluate the effect of biochar amendment rate and incubation time on soil chemical properties (Soil pH, Electrical conductivity, Soil exchangeable acidity, exchangeable Al, available P, and soil organic carbon).

Sub-objective 3: To investigate the effect of P sorption and desorption on acid soil amended with biochar at different incubation periods and amendment rates.

Thesis outline

The full thesis consists of five chapters describe succinctly as follows:

The general introduction of the thesis which discusses the general background of this research, the objectives, and the thesis outline.

Chapter 1 is a literature review that provides a consistent review on (i) Biochar (ii) soil acidity, its distribution in Cameroon, its consequences on plant nutrients (iii) phosphorus in soil, and, (iv) research gaps in biochar application to acid soils in Cameroon

Chapter 2 comprises of (i) reagents used in this research (ii) sampling of soil and biomass for biochar preparation and characterization (iii) experimental design amendments studies and chemical characterization (iv) sorption/desorption studies on the amended soil samples and (v) experimental protocols for analysis of some species in soil extracts and (vi) the description of the statistical tools.

Chapter 3 presents results and discussion. It is to fulfill three main aims which include: (i) Characterisation of sampled soil and prepared biochar; (ii) Analysing the effect of biochar amendment on the chemical properties of the sampled acid soil; and (iii) Study of phosphorus sorption and desorption in acid soils amended with biochar.

The general conclusion and perpectives which provides (i) A general run through of the main achievements of this study and (ii) Some research perspectives and recommendations.

It is completed at the end with references followed by an annex that contains a list of publications, a list of abstracts, posters, presentation at conferences, and a list of prices won.

CHAPTER 1

LITERATURE REVIEW

This chapter provides a consistent review of (i) Biochar (ii) soil acidity, its distribution in Cameroon, its consequences on plant nutrients (iii) phosphorus in soil and its availability study, and (iv) research gaps in biochar application to acid soils in Cameroon

1.1 An overview on biochar

An alternative option to overcome soil limitation recently has been the application of biochar. Biochar application is acid advocate as a multiple-win strategy which includes: soil fertility enhancement; pollutant immobilization; carbon sequestration; waste disposal [35–37].

1.1.1 What is biochar?

There exist several definitions for biochar. Biochar is a material derived from thermal decomposition of organic material under limited supply of oxygen,at a relatively low temperature (< 700 °C) [20]. Also, biochar can be defined as char co-product from the thermochemical processing of biomass utilized as a soil amendment and/or carbon sequestration agent [38]. Sohi in 2012 [39], defined biochar as a carbon-rich solid obtained by heating biomass, such as wood, manure with little or no oxygen (pyrolysis or ‘‘charring’’), which can be applied to soil for both agricultural gains and mitigate climate change. A standardized definition of biochar was brought up by the International biochar initiative (IBI), which define biochar as “a solid material obtain from the thermochemical conversion of biomass in an oxygen-limited environment” [40]. The specific properties, the inexpensive and environmentally-friendly nature has cause biochar to gain in interest and recognition.

The Scientometric review of biochar research in the years 1998-2018 reveal a total of 6934 documents in the field of biochar [41]. The number of publications for each year and cumulative numbers of publications are presented in Figure 1. This fully shows the increase interest of the scientific community on biochar research. The increase interest are in multidisciplinary domains such as mitigating global warming, soil amendment, enhancing soil fertility and crop yield, carbon storage, removal of organic and inorganic pollutants from aqueous solution.

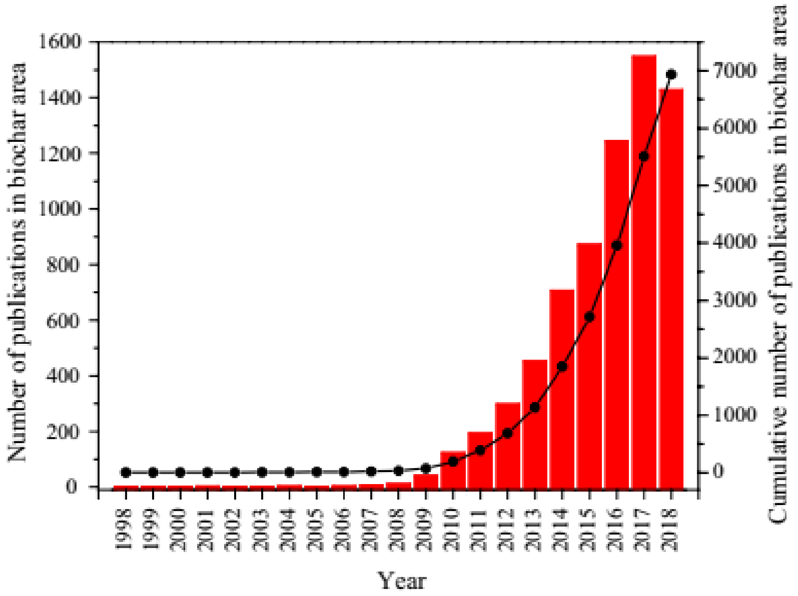


Figure 1: Publication output performance during 1998-2018[41]

Biochar vary in chemical and physical properties based on the biomass type and carbonization process conditions (pyrolysis production technique and temperature) [42]. The physical properties of the biochar affect many of the functional roles that they play in environmental management applications [43]. Apart from carbon, hydrogen and oxygen as major elements, it also contains nitrogen and sulphur. The physicochemical properties of biochar differ from the feedstock.

1.1.2 Biomass for the production of biochar

Biomass is a complex biological organic or non-organic solid product derived from living or recently living organism and available naturally. In Cameroon, various types of biomass source exist, namely agricultural crop residues, forestry residues, wood waste, municipal waste and manure. The majority of Cameroonian use biomass for cooking and the estimate for national access to clean cooking solutions is 23 %. Also, biomass constitutes 66.7 % of national energy consumption [44]. Most agricultural residues are obtained from cash crops (coffee husk, cocoa pods husk); food crops (rice husk, plantains and cocoyams pealings). As a result of it abundance and low cost of these residues, it can be used as a feedstock for the production of biochar. Conversion of these biomasses into biochar can be an economic advantage to local farmers and a better means of disposing agricultural waste. Biomass made up of cellulose, hemicellulose, lignocellulose and some extractives makes the biomass good for the production of biochar [45].

- ***Agricultural waste (Coffee husk and Cocoa pod husk)***

  - ***Coffee husk***

Coffee is a genius of flowering plants in the family Rubuaciae. Coffee species are shrubs or small trees native to tropical and southern Africa and tropical Asia. The Seeds of some species, called coffee beans, are used to flavour various beverages and products. The fruits, like the seeds, contain a large amount of caffeine, and have a distinct sweet taste and are often juiced [46]. There are over 120 species of *Coffee*, which is grown from seed. The two most popular are *Coffee arabica* , which accounts for 60–80% of the world's coffee production, and *Coffee canephora* (known as "Robusta"), which accounts for about 20–40% [47]. Coffee production distributions in the world include South America, Central and East Africa and Asian countries. According to the world atlas, there are 51 main exporters of coffee beans with the first three been Brazil, Vietnam and Columbia. In Africa, Ethiopia is the first exporter country with Cameroon rank number 21 with 34 200 metric tons [48].

Coffee processing generates significant amount of agricultural waste, ranging from 30 % to 50 % of the total weight of the coffee produced, depending on the type of processing [49]. The most important residues obtain from processing coffee are coffee pulp in the humid method and coffee husk in the dry method [50].

Dry processed coffee husks have moisture contents ranging from 7 % to 18 %; such an extensive range is attributed to variations in the processing and storage conditions [51]. Coffee husk is rich in organic matter, nutrients and contains compounds such as caffeine, tannins, and polyphenols. Because of the presence of the latter compounds, these residues have a toxic nature that not only adds to the problem of environmental pollution but also restricts its use as animal feed. Caffeine, one of nature's most powerful stimulants, is present in coffee husks at approximately 1.3% concentration [52]. Generally coffee husk contains about 24.5 % cellulose, 29.7 % hemicellulose and 23.7 % lignin [53].

Coffee husk utilisation can be classified in the following ways as review by Oliveira and Franka in 2015 [54]: (i) Industrial uses; (a) in ceramic industries; (b) in particle boards production; (c) flavour production; (ii) Fuel production; (a) used as solid fuel; (b) used in gasification; (c) In ethanol production; (iii) Adsorption of contaminants; (iv) Products obtain from fermentation; (a) production of organic acids; (b) production of enzymes; (c) bioactive compounds; (d) production of dietary fiber; (e) production of anthocyanins and (v) Agricultural application; (a) production of livestock food; (b) mushroom bed; (c) Biochar; and (d) silage and composting. Figure 2 shows a coffee tree plant and coffee husk.

Figure 2 : Coffee plants with coffee beans (left) and dry coffee husk (right)

- **Cocoa pods husk**

The cocoa plant is a small tropical tree with fruits of about 15-30 cm in length and 8 – 10 cm in diameter containing seeds in distinct rows, embedded in a soft pulp. The four main varieties of cocoa beans are the *Forastero cocoa*, *Crillo cocoa*, *Trinitario cocoa* and the *nacional cocoa* [55]. According to the international Cocoa organisation quarterly bulletin of cocoa statistics in 2021, Africa has the highest production rate of about 75.2 %, 19 % for Americas and 5.8 % in Asia and Oceania [56]. From the same bulletin, Cameroon is third Producing country (280 000 tons) with Ivory Coast the first. Cocoa is a highly competitive and lucrative commercial cash crop regarding income generation amongst other agricultural activities in the global markets. In Cameroon most cocoa farms are own by small holders with their plantations disseminated across the country, mostly in the Centre, South, South west and West. Cocoa in Cameroon generates a total of € 400 million (F CFA 260 000 000 000) and contributes to the national GDP by 1.2 % [57].

Cocoa pod husk is the main by-product from the cocoa industry constituting 67-76 % of the cocoa fruit (*Theobroma cacao* L.) weight [58]. The cocoa fruit consist of the husk, the pulp, the beans and the bean shells.

Cocoa pod husk comprises the epicarp, mesocarp, sclerotic part and endocarp. The Chemical composition of an example of a CP from Ghana consist primarily of fibrous materials including 19.7 - 26.1 % cellulose, 8.7-12.8% hemicellulose, 14-28% lignin and 6.0-12.6 % pectin. The epicarp is enriched with lignin, while the mesocarp contains mainly (~50%) cellulose and the endocarp is rich in pectic substances [59]. The ash content of cocoa pod husk ranges from 6.4-8.4% w/w with a variety of minerals. Significantly high amounts of K (2.8-3.8% w/w) are observed, followed by Ca, Mg and P [60]. Cocoa pod husk is also a source of phenolic acids, ranging from 4.6 to 6.9g GAE/100g

Campos-vegas and collaborators [58] review the main domains of use and application of cocoa pod husks, which are; (1) Food industry for obtention of flavour and aroma, production of vegetable gum, as texturizing agent, as preservative of odour, colour and aroma and encapsulation of probiotics. (2) Fuel Industry as substrate of ethanol production, catalysts for biodiesel and production of charcoal, fuel and non-condensable gas. (3) Dermatology/cosmetic industry for skin whitening, skin hydration, sun screening and wrinkles reduction. (4) Medical/pharmaceutical industry for the production of potash, synthesis of nanoparticles against multidrug resistant clinical bacteria (5) and various other applications including lipase obtention. Figure 3 represent a cocoa tree and cocoa pod fruit.

Figure 3 : Cocoa plant (left) and fresh cocoa pod fruit with illustration of parts (right)

1.1.3 Biochar production technologies

The production of biochar from organic materials includes the following processes, pyrolysis, gasification, hydrothermal carbonization, and flash carbonization technology.

- ***Pyrolysis technology***

Pyrolysis is a thermochemical process in which biomass is thermally degraded in its chemical constituents under inert or very low stoichiometric oxygen atmosphere [61]. Pyrolysis technologies can be differentiated by the reaction time of the pyrolysis material (e,g, slow and fast pyrolysis processes) and the heating method (e,g. pyrolysis process by burning of fuels, by electrical heating or by microwaves) [62]. Meyer and collaborators [62] indicated that pyrolysis comprises two stages known as the primary pyrolysis and secondary pyrolysis. Primary pyrolysis involves the cleavage up and de-volatilization of the biomass into its main constituents by the effect of heat. In this process, the dehydration, decarboxylation and dehydrogenation of the biomass take place. The secondary pyrolysis takes place after the primary pyrolysis and involves the cracking of heavy compounds which converts the biomass to char or gases like CH_2, CH_4, CO and CO_2. Some volatile molecules get re-condensed into aqueous phase called bio-oil.

Depending on the operating conditions, pyrolysis can be categorized into six subclasses, based on their main features, operating conditions, advantages, limitations.

- **Slow pyrolysis**: it is characterised by slow heating rate and long residence time. The pyrolyse temperature ranges between 550 – 950 °C with a heating rate of about 0.1 to 1 °C/s [61]. Slow and long residence time favours the formation of char but liquid and gaseous products are also formed in small quantities.

- **Fast pyrolysis**: This process is done at temperature of 850–1250 °C with a heating rate of 10–200 °C for a short span of time varying between 1 and 10 s. A typical fast pyrolysis produces 60–75% of liquid product, 15–25% of biochar and 10–20% of non-condensable gaseous products [63]. Fast pyrolysis process nowadays is being employed in the production of food flavours.

- **Flash pyrolysis**: This can be considered as an improved or modified form of fast pyrolysis. In flash pyrolysis, the temperature varies between 900 and 1200 °C and the heat pulse given to the biomass last for a very short time (0.1 to 1s) [64].

- **Vacuum pyrolysis**: This is the degradation of biomass under low pressure and in the absence of oxygen. In this process, the pressure range during the vacuum pyrolysis is usually 0.05–0.20 MPa and the temperature is kept between 450 and 600 °C [65]. The vacuum pyrolysis, tend to improve the porosity of the biochar and develops several micro-porous/macro-porous structures [66].

- **Intermediate pyrolysis**: The pyrolysis operating condition in this process is between fast pyrolysis and slow pyrolysis. Intermediate pyrolysis operates between 500 and 650 °C, with heating rate ranging between 0.1 and 10 °C/min with residence time of 300– 1000 s. The typical product contains 40–60% liquid, 20–30% non-condensable gases and 15–25% biochar [67].

1.1.4 Biochar characterisation with relevance to soil application

Characterisation of the physical and chemical properties of biochar is of great importance in determining their potential applications. The physical and chemical properties of biochars produced from different biomass and production conditions vary greatly [28], thus it agronomic potential and environmental uses. Some physical and chemical properties of biochar are discussed below.

- **Biochar yield**

The yield of biochar is the percentage of biochar at the end of production. It is determined by simply calculating the percentage of the ratio of the dry mass of biochar to dry mass of precursors [28]. Generally higher biochar yield are obtained at lower pyrolysis temperature (< 500 °C) which is mostly due to minimal condensation of aliphatic compounds, and lower losses of CH_4, H_2 and CO [68]. At higher temperature (above 500 °C), the decrease in yield is due to dehydration of hydroxyl groups and thermal degradation of lingo-cellulosic structures [69]. Coffee husk produced by Domingues and collaborators [70] at pyrolysis temperature of 350 °C had a percentage yield of 43.5 % and at higher temperature : 50 °C, 31.6 %.

The yield of biochar also depends on the biomass type which is due to the variation of lignocellulosic component and ash content on the biomass [71]. During pyrolysis, organic materials begin to undergo thermal decomposition at 120 °C, hemicellulose degrade at temperature between 200 °C and 260 °C, cellulose from 240 °C to 350 °C, and lignin between 280 °C and 500 °C. Therefore, the proportions of these components in the organic waste may influence the degree of reactivity and hence, the degree to which the physical structure is modified during the processing [43].

Another factor that affects the yield of biochar is the residence time. Generally, a long residence time decreases considerably biochar yield. This trend has been demonstrated by Rehrah and collaborators [28] whereby a continual decrease in yield was observed with increase residence time. This was attributed to the release of volatile matter [72].

Apart of the temperature of pyrolysis, the chemical composition of the biomass has a direct impact on the nature of the biochar produced and the yield percentage.

- **Ash content**

The ash content of biochar is the inorganic component in the biochar after loss of some of the organic component. The ash content of the biochar is determined by heating a weighed sample of the biochar in a muffle furnace at 760 °C for at least 6 h; the ash content percentage is determined by calculating the percentage of the ratio of the mass remaining solid in the crucible to the original mass of the biochar [28].

Ash content is largely determined by feedstock origin [73]. The mineral content of the feedstock largely influences the ash content percentage when there is a gradual loss of carbon, hydrogen and oxygen during processing [74]. Coffee husk in recent works gave a high level of ash content due to high potassium content of the biomass[70].

Biochar with high ash content can have a liming application to correct soil acidity due to it rich nutrients and high alkalizing capacity [75].

- **Biochar pH**

Biochar pH is one of the chemical properties that are routinely measured for biochar application of soils. Summarised past work briefly describe the determination of biochar pH as follow; The biochar pH are measured in the ratio 1:5, 1:10, and 1:20 biochar: water ratio shaking, and 1:20 biochar:water ratio after 24 h shaking on a reciprocating shaker. After this, samples are allowed to stand for 30 min and the pH measured using a pH meter [76]. The recommended procedure for biochar pH measurement is done by using the biochar:water ratio 1:10 and shaking for 1h, then the suspension is left to stand for 30 min before introducing the pH electrode for pH measurement [76].

Most biochar used for soil amendment are alkaline [77]. The high pH values of biochar is due to the removal of the acidic functional groups during carbonisation and the enrichment of ash content which contains alkali and alkali earth metals [78]. Biochar produced at higher temperature results to higher biochar pH due to the formation of basic surface oxides, carbonates and hydroxides [79]. The pH of biochar depends on feedstock and the pyrolysis temperature [80].

The potential consequence of the application of biochar with high pH is to increase soil pH, decreases Al^{3+} toxicity, and reduce Fe and Mn availability [81]

- **Biochar Electrical conductivity**

The electrical conductivity (EC) is linked to the quantity and nature of salts dissolved in solution and is the most widely used soil salinity test [82]. Biochar electrical conductivity gives an understanding of the amount of soluble salts in a soil solution. Biochar EC is important to be determined because high rates of biochar application to the soil may adversely affect salt-sensitive plants [83]. In the determination of biochar EC, the ratio of biochar to water in the suspension affects the EC value. A review of past research work describes the determination of biochar pH as follow. The biochar electrical conductivity was measured in 1:10 and 1:20 biochar:water ratio and shaken for 1 h; then the samples were allowed to stand for 30 min before the EC is measured with an EC meter [76]. The recommended procedure for biochar EC measurement is done using the biochar:water ratio 1:10 and shaken for 1 h, then the suspension is left to stand for 30 min before introducing the EC electrode for pH measurement [76].

Biochar EC is dependent on the feedstock and the pyrolysis temperature. Cantrell and collaborators [84] reported that biochar produced at higher pyrolysis temperatures generally have high EC values, which was attributed to increase ash content .Domingues and co-workers [70] reported high EC for biochar produced from coffee husk which was due to the presence of soluble minerals. The mineral content of the biomass can result to a biochar with high ash content which will influence the value of biochar EC [28].

Biochar EC has as agronomic potential to supply Ca and K to the soil solution and thus to replace conventional sources of K and Ca [70].

- **Acid-neutralizing capacity**

The acid-neutralising capacity (ANC) refers to the amount of acid consumed in cmolkg^{-1} when the biochar is found in the acid medium. It can be an indication of the quantity of H^+ the biochar can consume in soil solution. The ANC of biochar is determined by mixing 0.5 g of biochar with 0.05 M HCl and 0.1 M $NaNO_3$ and shaking for 24 h. The equilibrated solution is then filtered and titrated against 0.05 N NaOH and 0.1 M $NaNO_3$ solutions [85].

The ANC of biochar is related to its alkalinity. It takes into account the ash content and the basic functional groups ($-O^-$ and $–COO^-$) found at the surface of the biochar [86]. Cocoa shell biochar has a high ANC of 217 cmolkg^{-1}, which gives cocoa shell biochar a large potential to act as a liming agent [85]. Research work done by Cornelissen and co-workers [87], concluded that the primary cause of increased in crop production in an Ultisol of the humid tropics due to biochar addition was related to its acid neutralising capacity.

- **Biochar liming potential**

The liming potential of a biochar is often reported as an equivalent proportion of the liming effect that $CaCO_3$ would have. The review of the procedure to assess the liming potential of biochar include: (a) the measurement of calcium carbonate content of the soil such as those of Rayment and Lyons [88] as suggested by IBI [40], which involve the treatment of a known mass of the biochar with a known volume and concentration of HCl. The excess acid after the reaction of the biochar and the acid is back-titrated with a standardize base; (b) the measurement of the pH buffering capacity of the soil [89,90]. It is done by adding incremental amount of either a base or an acid depending on the initial soil pH, then letting the soil incubate for a specific period of time [91] and establishing a titration curve. The soil pH buffering capacity is calculated from the slope of the titration curve as reported as the quantity of base/acid required to raise/decrease the soil pH by one unit [92,93]. The recommended procedure for measurement of biochar liming potential: calcium carbonate equivalent is mostly determined by Rayment and Lyons method[88] due, to the fact that the pH buffering capacity method is time consuming.

Biochar liming potential is dependent on the biochar type and production conditions. Biochar from coffee husk and cocoa pod husk were reported to have very high liming values which was related to the high mineral concentration specifically calcium and potassium carbonates [70]. The higher liming values are regulated by biochar ash content and the chemical composition and to a lesser extent the biochar pH. Liming potential of biochar should be considered when used as amendments with aim at correcting soil acidity.

- **Biochar alkalinity**

Alkalinity is one of the most influential biochar properties, because changes in pH have cascading impacts on soil processes, including nitrogen mineralization, mineral precipitation, ion exchange and greenhouse gas emissions [94]. Four broad categories of biochar alkalinity have been identified in the literature: surface organic functional groups, soluble organic compounds, carbonates, and other alkalis which may include oxides, hydroxides, sulphates, sulphides, and orthophosphates [95]. Nowadays many methods are used to determine biochar alkalinity: (1) directly titrating a biochar water slurry with 0.1 M HCl [96]; (2) equilibrating biochar with 0.03 M HCl and titrating the filter extract with NaOH [97]; (3) shaking biochar with 1 M HCl for 2 h. followed by the titration of extracts with NaOH [95].

Feedstock, pyrolysis temperature, and other pyrolysis conditions affect total biochar alkalinity and relative proportions of biochar alkalis. Inorganic alkalis consistently constituted the majority of total lignocellulosic biochar alkalinity, emphasizing their importance in pH-sensitive biochar research [98]. Fidel and collaborators[98] showed that wood biochar consistently had a higher proportion of carbonate alkalinity than corn biochar, whereas corn stover biochar consistently had a higher proportion of non-carbonate inorganic alkalinity. Yuan and Xu [97] demonstrated that the liming effects of nine biochar samples on soil acidity correlated with alkalinity with a close linear correlation between soil pH and biochar alkalinity. Biochar with higher alkalinity makes a better choice to be used as soil amendments to acid soils.

- **Fourier Transform Infra-red spectroscopy**

Fourier-transform infrared (FTIR) spectroscopy have been widely used for characterisation and monitoring of biochar and organic matter in soils [99]. Vibrational spectroscopy has provided a great deal of information about the structure, bonding and reactivity of biochar. FTIR analysis of soil constituents including soil organic matter and biochar has been obtained using a broad array of sample presentation methods. The main methods include diffuse reflectance (DR-FTIR), attenuated total reflectance (ATR-FTIR), transmission methods (deposited material on IR transparent materials, pressed KBr pellets, self-supporting films) and photoacoustic (PAS-FTIR) spectroscopy [100].

The functional groups and structure of biochar as can be analysed using the FTIR depends on feedstock type, pyrolysis temperature and the presence of inorganic structure. Biochar produced at higher temperatures are characterised by predominantly persistent carbon and have increased stability with increasing aromatic character [101]. Johnston [100] in the book "a guide to analytical methods", illustrated the influence of temperature on the FTIR spectroscopy of biochar produced at different temperatures. The main discernable changes are observed in the $\upsilon_{(C\text{-}H)}$ region. For low temperature biochar, $\upsilon_{(C\text{-}H)}$ region is dominated by aliphatic $\upsilon_{(C\text{-}H)}$ with little contributions from aromatic $\upsilon_{(C\text{-}H)}$ while at high temperature; the aromatic $\upsilon_{(C\text{-}H)}$ bands are completely dominant. This is attributed to the condensation of the aromatic structures present. Other discernable bands such as $\upsilon_{(C=O),}$ $\upsilon_{(C\text{-}H)}$, $\upsilon_{(C=C)}$ vary in intensity with variation of temperatures. Biochar also present intense picks associated with mineral/inorganic impurities they contain. The FTIR features of carbonates are well known, with a strong broad band at 1447 cm^{-1}, and sharper bands at 877 cm^{-1} and 713 cm^{-1} are appears in biochar produced at temperature above 500 °C [86].

The functional groups (alkyl functionalities) show a strong correlation ($R^2 = 0.87$; $p < 0.001$) with it hydrophobicity [102] and the presence of inorganic component on biochar can be a source of nutrients or alkali and alkali metals.

- X-ray diffraction

X-ray diffraction (XRD) is a non-destructive technique that is widely used to identify crystalline solids in a mixture with other crystalline or amorphous phases [103]. The XRD pattern of most biochar shows a broad hump centred at around 3.8 Ȧ due to scattering of X-ray by amorphous carbon and sometimes amorphous silica [104]. Apart from the broad hump present in most XRD sprectrum of biochar, sharps peaks are also present indicating the presence of inorganic minerals like calcite, quartz, sylvite, etc. The density of these sharp peaks is dependent on the pyrolysis temperature and biochar source.

The common mineral found in biochar is calcite with sharp intense peaks at 3.85, 3.03, 2.49, 2.28, 2.09, 1.91 and 1.87 Ȧ. Calcite is mostly found in biochar of coffee husk, cocoa pods, chicken manure, wheat straw, eucalyptus feedstock [70,95,105]. Calcite is the major constituent in ash derived from many feedstock and biochar [106]. It is form by the combustion and carbonation of calcium oxide [107]. The formation of carbonates in biochar is due to the entrapment of CO_2 evolved from thermal decomposition of organic C during slow pyrolysis in the alkaline charred material [104]. Some biochar produced at low temperature has whewellite minerals ($Ca(C_2O_4).H_2O$), but with increase in temperature (to about 550 °C), the mineral is converted to calcite [108]. The X-ray analysis of some biochar reveal other minerals like sylvite (KCl), magnesite ($MgCO_3$), bassanite ($CaSO_4.0.5H_2O$) and apatite ($Ca_5(PO_4)_3(OH,F,Cl)$ which is due to plants rich in chloride, sulphate and carbonate [109]. Some biochar contain huge amount of quartz minerals which can be due to the high contain of Si in the feedstock [110] or from soil contamination of the feedstock.

The XRD analysis gives knowledge of the crystalline phases which is useful for predicting their solubility, and biological availability. The release of Ca from the dissolution of whewellite and calcite makes them more available in soil solution. The progressive release of phosphate from biochar which contain apatite crystals can be a source of slow release of phosphorus in to the soil solution.

- **Scanning electron microscope (SEM)-electron diffraction spectroscopy (EDS)**

SEM-EDS is an effective way to study structural characteristics of biochar as well as to study it chemical properties [111]. Thies and Rillig [112] showed that the microscopic physical structure of biochar is one of the key properties related to the effect on soil properties conditions, and the surface area of the pre-charred source material which greatly enhance its water holding capacity.

The trend in the SEM images of biochar varies with pyrolysis temperature [113] and feedstock type [114]. The morphological analysis of biochars show many pores and cracks on the surface and rough structures. The number of pores on biochar increase with pyrolysis temperature while the pore size becomes smaller [111]. This can be explained by the fact that at lower pyrolysis temperature some fibers are still present but at higher temperatures, the fibers disappear by combustion. The rough structure is mainly due to the degradation of partial lignin component [78]. The image of biochar at times presents white dots which are formed by the degradation of the cellulose component and its precipitation and growth as sphere [115].

The EDS analysis which is mostly coupled to SEM is used for the determination of elemental content on selected points and on selected surface areas with subsamples. Researchers have used this technique to evaluate the O/C ratio of biochar produced at different conditions [111]. Increase in C and decrease in O with increase pyrolysis temperature due to increase in degree of carbonisation and dehydration reaction [116].

- **Available phosphorus determination**

Many studies have reported biochar as being a potential source of P [117,118]. Essential macronutrients P retained in biochar could be release and made available to plants, enhancing plant growth [119].

In order to assess the amount of P in biochar, several experimental procedures have been proposed depending on the form of phosphorus to be determined. Some studies include (i) the sequential batch leaching experiment with deionized water (H_2O-P) [117,119], (ii) the column leaching experiment in deionized water [118], (iii) Total phosphorus extraction by digestion in 10% HCl, 10% HNO_3 (v/v), 2 % formic acid extractable, 2 % citric acid extractable P and 1 M neutral ammonium citrate extractable P [26] (iv) phosphorus availability can also be extracted with 0.5 M H_2SO_4 and 0.5 M $NaHCO_3$ (pH = 8.5, Olsen P) [120].

The phosphorus in biomass feedstock almost completely retains in biochar in the pyrolysis process. Kim and collaborators [121] found that the feedstocks with abundant P could generate the P-rich biochar. In addition, the pyrolysis temperature of feedstock is another important parameter of affecting the nutrient contents of biochar [122,123]. Previous studies indicated that the content of total P in the biochar increased with the pyrolysis temperature [124]. When the pyrolysis temperature is above 700–800 °C, the P in biochar will lose and stabilize as insoluble forms. Phosphorus in biochar exist in inorganic orthophosphate and pyrophosphate [125].

Knowledge of the amount of available P in biochar is essential to determining the rate to be applied to meet crop P requirement, while ensuring a low risk of water eutrophication [126].Hale and co-workers [127] reported that the amount of P released after 60 d equilibrium period was 1483 ± 45 mg/kg and 172 ± 1 mg/kg for the cacao shell and corncob biochars. About 9.79 mg/kg and 13.87 mg/kg of available P from CH biochar pyrolyse at 350 and 500 °C (Olsen extraction) was reported by Dume and collaborators [128]. Other studies reported that rice straw and canola stalk biochars prepared at 650 °C contain Olsen P of about 1.09 g/kg and 1.18 g/kg respectively [120].

1.1.5 Biochar application

The use of biochar for energy and as agricultural amendment is not a new idea: the transformation of biomass material into black solid has been documented back to the beginning of modern science and there exist archaeological evidence of even older application [129].

- **Application in agriculture**

Past research on the application of biochar to the soil has shown its ability to improve the soil quality. The application of biochar influences the chemical properties of acidic soils and also influences the sorption and desorption of available P in the soil solution [24,32]. Hossain and collaborators [130] reveal that alkaline biochar added to soil increases the cation exchange capacity (CEC). Application of biochar in the soil can be a source of long-term carbon storage to minimize climate variation by enhancement in the biogenic C collection, decrease greenhouse gas emissions [131], restore soil fertility [132]. The pore structure, surface area and mineral matter are affected by biochar [133], reduces N emission and leaching [134], thus enhancing crop yield and productivity.

- **Remediation of organic and inorganic contaminant in soil and aqueous medium**

The various research reports in recent years have found biochar to have the ability to remove organic pollutants from soil, water and sediments, and thus lowering their bioavailability and preventing toxic substances transferring from environment to plant and further to organisms including human. Biochar properties such as its micro porous structure, active surface functional groups, high pH and CEC, FTIR, XRD, SEM/EDS and TEM analyses makes its favourable for immobilization due to its strong affinity for heavy metals cations, anions and neutral organic substances [135–137].

Biochar has been evidenced to act as an efficient sorbent of various contaminants, organic and inorganic, because of its huge surface area and special structure [138]. Jiang 2012 [136]has shown effective reduction of Cu, Pb and Cd in contaminated soil systems after application of biochar. Beesley and Marmirol [139] explored the capability of biochar to immobilize and retain As, Cd and Zn from a multi-element contaminated sediment derived soil with microanalyses techniques, which showed that biochar reduced the concentration of Cd and Zn with 300- and 45- fold, respectively, but the leachate concentration was not reduced. With the immobilization of heavy metals in the soil, heavy metals can be retained in the soil and will release in a slower rate which exerts less impact on the environment and will decrease uptake by plants [138]. Wang and collaborators [140] examined the sorption of the terbuthylazine in biochar-amended soils and found that the adsorption coefficient increased by 63 and 2.7 times in the biochar 700 and biochar 350 biochar amendment soil respectively. Results showed that 2-14% sulfamethoxazole was found to transport through soils with biochar amendment versus 60% in the leachate of soils without biochar amendment [141]. Tan and collaborators [137] wrote an extensive review on the application of biochar for the removal of pollutants from aqueous solutions, in which the production of biochars reveals a wide variety of biomass materials have been used as the feedstocks and pyrolyzed by different processes to tackle water pollution. According to the available literatures about biochar application in water treatment, nearly 46% of the studies concerned the removal ability of biochar for heavy metals, 39% for organic pollutants, 13% for NP, and 2% for other pollutants [137].

In water system, water-soluble arsenic and ammonia has been recovered on biochar surfaces [142,143]. Research work has shown that both sludge- and poultry manure-based biochar was efficacious for the removal of low levels of cations and anions in municipal and industrial waste [144]. Phosphate, nitrates has been effectively sorbed from water solutions [145]. The effective removal of organic compounds by biochar was ascertained many researchers. Phenanthrene strongly sorbs onto biochar [146], hexachlorobenzene [147], sulfamethoxazole [141] and substantially reduced the availability of PCDD/Fs measured by polyoxymethylene (POM) passive uptake and earthworm (*E. fetida*) uptake [148]. Moreover, for pesticides, biochar has shown a remarkable efficacy in the elimination of pesticides such as isoprotuton [149], benzonitrile [150], and herbicies such as (4-chloro-2-methylphenoxy)acetic acid, atrazine and trifluralin in soil [151,152].

The mechanism involved in the removal of inorganic and organic contaminants from soil and aqueous medium is based on the intrinsic properties of the biochar. Higher temperature biochars possess high pH, CEC and surface area [153] while low temperature have higher numbers of actives sites and the existence of stable carbon-oxygen complexes [154]. The presence of the carbon-oxygen on the surface of biochar is important for sorption/chemical reactions potentials [139]. Mechanism involve in the removal of inorganic contaminants include adsorption, reduction, oxidation [155]. The type of pores on the biochar (macro, micro and nanoporous) aids the reduction of metals into less mobile species [143] as the case of microscopic grapheme moieties in biochar which serve as both adsorption and redox reaction due to their high affinity for contaminants and the ability to transfer electrons to adsorbed reactants [156]. The presence of functional groups are involve for the removal of Cr and Pb complexation [157]. The main mechanism involve in the remediation of organic contaminants onto biochar is adsorption, combine with immobilization and degradation [158]. Also higher temperature biochar has higher adsorption capacity on Trichloroethylene adsorption which was attributed to their high aromaticity and low polarity [124]. Others factors such as pyrolysis temperature can also affect the physicochemical properties of biochar which further influences the adsorption capacity of biochar [159]. The summary proposed mechanism for adsorption of (a) heavy metals and (b) organic contaminants adsorption of biochar are illustrated by the figure below

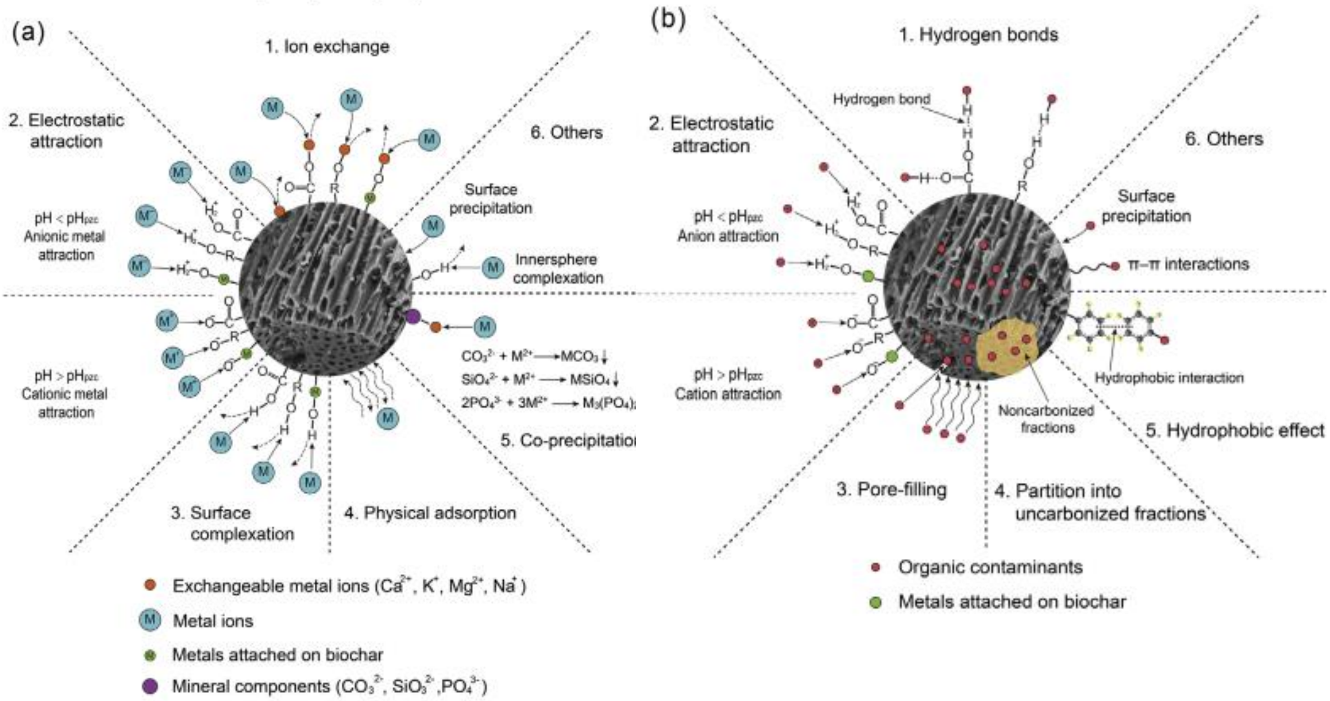


Figure 4: Summary of proposed mechanisms for heavy metals contaminants adsorption on biochars[137]

Biochar is seen to be beneficial in alleviating climate change, improving crop productivity, remediating polluted environment and recycling agricultural wastes according to most of the published literature. The benefits of biochar are multiple, intertwined and include both direct and indirect effects. The various benefits of biochar are all linked with one another and they would form a virtuous circle once one aspect is triggered. Therefore, biochar can be potentially an attractive alternative in modern society to solve environmental and food problems faced by the rapid developing society and rapid increasing population. Usage of biochar in a right way, e.g., appropriate biochar and dose in a certain soil, can bring win-win consequences.

1.1.6 Potential risk of biochar

Previuos research work on biochar application has look into its potential risk in the soil and waste water treatment. When applying biochar, stability is an important property. Huang and collaborators [160] reported the potential dissolution of organic matter from biochar in complexation of heavy metals, suggesting that dissolved organic matter form biochar can be found in solution due to instability of biochar. In addition, biochar, especially derived from sludge, contains heavy metals, which may be leached during the process of water and wastewater treatment, causing the heavy metals pollution [159]. Apart from stability of biochar, potential toxicity of biochar on microorganisms should be also paid attention to. A biochar-treated acid soil was evaluated for soil microbial communities by PLFA; where increased PLFA was observed compared to the control soil after 431 days of incubation [161]. It has been demonstrated that higher surface area of biochar could adsorb water, nutrients, and soluble C which in turn facilitate the microbial colonization [161]. Microorganisms which have the ability to degrade recalcitrant C compounds are likely to be predominant in biochar-amended soils [162,163]. A study conducted by Gong and collaborators [164], reported that low dose of biochar promoted enzymatic activities of soil microbes. For instance, evaluation of changes in dehydrogenase activity in biochar-amended/unamended soils is a good indicator for the evaluation of degree of recovery of degraded soils [165]. Thus, in view of the application of biochar, studies need to investigate the potential toxicity to the environment.

1.2 Soil Acidity

Soil acidity can be considered as the capacity of soils to manifest properties of acids or protons donors [166]. A soil is said to be acidic when the pH is below 6.5 [167]. Theoretically, soil acidity is quantified on the basis of H^+ and aluminium (Al^{3+}) concentrations of soils [168]. It occurs when acidity-generating processes outweigh acidity-consuming processes [169]. Soil acidity can decrease crop yields and is one of the limitations to agricultural productions.

1.2.1 Acid soil distribution

- **Distribution in the world**

Acid soils are distributed globally on two geographical belts (i) the northern belt which is dominated by podzols, and (ii) the southern tropical belt that consists in great percentage of Acrisols and Ferrasols [170]. Acid soils cover 30 % of the total ice-free land area and 50 % of potential arable lands of the world [171]; 75 % of these areas are also affected by subsoil acidity [172]. Sixty-seven percent of the acid soils support forests and woodlands and approximately 18% are covered by savannah, prairie and steppe vegetation [167]. The Figure 5 illustrates the world distribution of acid soil.

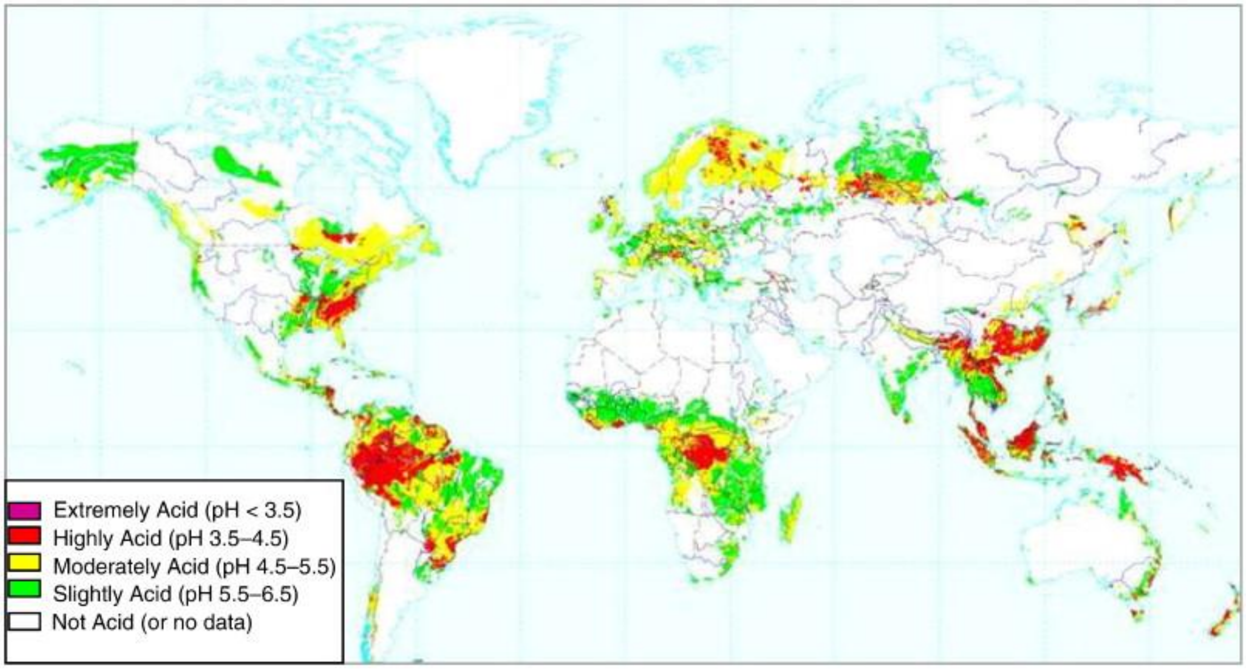


Figure 5: World distribution of acid soil [173]

- **Distribution in Cameroon**

Acid soils are widespread in Cameroon and it cover about 75% of agricultural land in the country [174]. The cartography of soils with pH below 5.5 is spread all over Cameroon. Table 1 gives a summary of soil pH values and their locations in Cameroon which shows that acid soils are widely spread in the Southern and Western regions of Cameroon. The acidic soil is due to relative enrichment in Fe, Mn, Al and Ti oxides coupled to high weathering rates reflect typical conditions of tropical soils [175].

Table 1: Some soil location and soil pH (pH <6.5) in Cameroon

Region	Location (Soil pH)	Reference
Centre	Mbalmayo (4.78), Akonolinga (Megang) (4.87) and Yaounde(Nkolbisson) (5.05), Bokito (4.72), Yaounde(Leboudi) (5.45) Minkoameyos (5.4),	[14,176–179]
Littoral	Douala (4.51), Edea (4.06). Nzock (4.7), Mbomi (4.9)	[178,180]
North West	Mbot (4.70), Nkambe (4.90), kishong(5.2), Bambui (4.9), Awing (4.62), Wum (4.8)	[176,178,180,181]
South	Nyangong, Ebom (4.59), Ebimimbang (4,59), Ngougoumou (4.13-4.75), Abang (4.5), Sangmelima (4.04), Ebolowa (4.09)	[178,182–184]
South West	Missellele (4.5), Tombel (5.07), Eastern flank of Mount Cameroon (4.7-5.6), Ekona (4.28), Limbe (5.95)	[6,178,185,186]
West	Baigom (4.90), koutaba (4.90), Mount Bamboutos area (4.9 – 5.1)	[176,187]

1.2.2 Soil acidification

Soil acidification is defined as a decrease in acid-neutralising capacity or an increase in base-neutralising capacity, resulting in an increase in acid strength as represented by a decrease in soil pH [188]. Soil acidification occurs naturally but can either be accelerated by certain plants and human activities or slowed down by careful management practices [189]. List below are the main causes of soil acidification.

- ***Acid parent materials***

Parent material from which soil horizons is from is an important factor that determines the content of the secondary minerals of soils [190]. Soils which contain granite are likely to be more acidic than soils containing limestone. In the tropics and sub-tropics, under rainfall and high temperature, the process of acidification occurs over a long or a short time with weathering of soil parent materials that releases significant amounts of aluminium, iron and silica [191]. In the humid tropics, most silicate minerals in the parent material are weathered away by desilication, leaving little other than the oxides of iron and aluminium

[172]. Some sedimentary rocks such as shale and coal are rich in sulfides, which, when hydrated and oxidized, produce sulfuric acid which is much stronger than silicic acid.

- ***Acid rainfall and leaching***

In climates where rainfall exceeds evapotranspiration, soils with low buffer capacity tend to acidify. Excess water infiltrating the soil enhances leaching of basic ions (calcium, magnesium, sodium and potassium) from the exchange complex of soil (clay minerals, humus) and their substitution by protons (H^+) and aluminium ions (Al^{3+}) [192]. This way, neutral clay may be converted into a hydrogen clay or acid clay, which gradually accumulates and intensifies under increasing amounts of rainfall.

- ***Organic matter decomposition***

During the mineralisation of organic matter, organic acids are due to the reaction of CO_2 produced in the process with water produced [193]. Like rainfall, the contribution to acid soil development by decaying organic matter is generally very small, and it would only be the accumulated effects of many years that might ever be measured in a field

- ***Nitrification of ammonium fertilizers***

Farms with high level of application of ammonium fertilizers tend to be acidic due to nitrification. Nitrification is a biological oxidation process with the need of nitrospira bacteria which mediate the entire reaction from NH_4^+ to NO_3^- within one organism in the complete ammoia oxidation to nitrate known as comammox [194]. The process releases hydrogen ions which increases the acidity of the soil.

$$NH_4^+(aq) + 2O_2(g) \rightarrow NO_3^-(aq) + H_2O(l) + 2H^+(aq) \qquad (1)$$

This acidity can only be neutralized if NO_3^- can be completely transformed back into the original input forms. However, some NO_3^- is usually leached through the soil profile along with charge–balancing base cations and thus acidity tends to remain in the system [195].

1.2.3 Consequences of soil acidification

The soil pH aids to identify the type of chemical reactions that are likely to be taking place in the soil. In this regard, the concerned of the effect of pH on the availability of toxic elements and nutrient elements is important.

- ***Aluminium toxicity***

Aluminium (Al) is the third most abundant element in the Earth's crust and is a primary constituent of many minerals in soil [196]. In normal conditions, Al exists in the form of silicates, phosphate, sulphides, and oxides in normal soil conditions. Upon acidification (when pH of soil drops below 6.5), aluminosilicate clays and aluminium hydroxide minerals release aluminium-hydroxy cations and $Al(H_2O)_6^{3+}$ and Al^{3+}, by dissolving and forms the mononuclear species $AlOH^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$ and $Al(OH)_4^{-}$ and soluble complexes with inorganic ligands such as sulfate and fuoride, AlF_2^{+}, AlF_3^{+}, and $Al(SO_4)_2^{+}$ [197,198]. Al^{3+} and $AlOH^{2+}$ are the most toxic chemical species of Al [199] to plants [200]. Al^{3+} has the tendency to form complexes with inorganic anions, including SO_4^{2-} and PO_4^{3-}, and organic anions (e.g., organic matter with carboxyl groups and organic acids) [196], thus reducing soil fertility.

Aluminium stress causes a series of morphological, physiological, biochemical, and molecular changes in growing plants reducing growth, development, and crop yield [201]. Soil aluminium concentration of 2-5 ppm is toxic to the roots of sensitive plant species and above 5ppm is toxic to tolerant species. Al^{3+} has multiple target sites such as root apex, nucleus, cell wall, plasma membrane, and cytoskeleton in root cell of plant to induce toxicity [196]. The biochemical and physiological aspect of Al stress in plants was review by Rahman and Upadyaya [201] in the following points (i) Aluminium stress affects water relation and osmoregulation; (ii) Aluminium in tress reduces root growth; (iii) Aluminium induces oxidative stress; (iv) Aluminium affects photosynthesis in green plants; (v) Aluminium has an impact on protein metabolism and (vi) Aluminium has an impact on enzyme activity. Thus, the plants which are not tolerant to Al stress will have a poor growth rate and low crop production.

- ***Phosphorus immobilization***

Soils suffering from aluminium toxicity are generally associated with phosphorous deficiency. The phosphorous-use efficiency in such soils is around 10–15% in the best situations [202]. In acidic soil solution, oxy-hydroxides of Al and Fe strongly bind to phosphate, immobilizing the phosphate for plants [203]. The immobilisation is through adsorption, precipitation and ligand exchange mechanism in which aluminium forms insoluble and stable complexes with inorganic and organic phosphates, forming highly insoluble phosphorus compounds [204]. Phosphate also bound to low phosphorous availability is considered to be one of the main limiting factors to plant growth in acid soils, in addition to human wealth in tropical areas [205].

- ***Soil fertility and crop production***

There is a growing recognition, among specialists and policy makers that soil acidity is a major constraint to crop production in humid tropical environments [206,207]. This is due to associated effects of Al and Mn toxicity, nutrients deficiency and their adverse effects on crop growth [168]. Complex interactions of plant growth-limiting factors due to soil acidity involves physical, chemical and biological properties of the soil [208]. The physical constraints for plant growth on tropical acid soils include soil erosion and water-holding capacity. Nutrients deficiencies are the major chemical constraints that limit plant growth on acid soils [209]. The biological properties include the adverse effect of acid soil on microorganism activities, which affect the decomposition of organic matter, nutrient mineralisation, immobilization, uptake and utilization by plants which has a consequence of crop yield and soil fertility [210].

Fageria and collaborators [211] reported that soil acidity has multiple implications for plant growth and fertility issues; it can lead to slow response to ammonium phosphate, stunted roots and plant growth and increased incidence of plant diseases and toxicity.

1.2.4 Amelioration of the quality soil acidity

Problem of soil acidification leads to low fertility status, thus many agricultural practices have been recommended to solve the problem.

- ***Liming***

Liming is the application of Calcium and/or magnesium carbonates, hydroxides, and oxides [212]. Liming is the most widely used long-term method of soil acidity amelioration, and its success is well documented [213,214]. Adequate liming eliminates soil acidity and toxicity of Al, Mn, and H; improves soil structure (aeration); improves availabilities of Ca, P, Mo, and Mg, pH, and N_2 fixation; and reduces the availabilities of Mn, Zn, Cu, and Fe and leaching loss of cations [168].

Liming from wood ash applied in the forest zone of Central Cameroonian soil raises soil pH, base saturation, and Ca and Mg contents [14]. Another study on the groundnut response to ash, and lime on southern Cameroon, reduced soil exchangeable aluminium and improved groundnut yield [215]. The changes in the chemical properties with the use of lime (dolomitic lime) can be explained equation (2), (3) and (4) [216].

$$CaMg(CO_3)_2 + 2H^+ \leftrightarrow 2HCO_3^- + Ca^{2+} + Mg^{2+} \quad (2)$$

$$2HCO_3^- + \ 2H^+ \leftrightarrow 2CO_2 + 2H_2O \quad (3)$$

$$CaMg(CO_3)_2 + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \quad (4)$$

The above equations show that acid-neutralisation reactions of lime occur in two steps. In the first step, Ca^{2+} and Mg^{2+} replace H^+ on the exchange sites of clay or organic matter, formingHCO_3^-. In the second step, HCO_3^- reacts with H^+ to form CO_2 and H_2O to increase pH.

Bolan and co-workers [203] reported that in variable charge soils, a decrease in pH increases the anion exchange capacity, thereby increasing the retention of P. Ngane and co-workers [185] reported an increase in Bray-2 available P with liming, up to a pH value of 8 in South-Western Cameroonian acid soil and then decrease at higher pH values. This observation was also mention in Brazilian oxisol [217]. Thus liming also improve phosphorus availability to a certain extent.

Increase in availability of P in the pH range of 5.0 to 6.5 was associated with release of P ions from Al and Fe oxides, which were responsible for P fixation [218]. At higher pH (>6.5), the reduction of extractable P was associated with precipitation of P as Ca phosphate [219]. These increases in extractable P or liberation of this element in the pH range of 5.0–6.5 and reduction in the higher pH range (>6.5) can be explained with equation (5) and (6).

$$AlPO_4(P\ fixed) + 3OH^- \leftrightarrow Al(OH)_3 + PO_4^{3-}(P\ released) \quad (5)$$

$$Ca(H_2PO_4)_2(soluble\ P) + 2Ca^{2+} \leftrightarrow Ca_3(PO_4)_2(insoluble\ P) + 4H^+ \quad (6)$$

Studies have shown that liming materials affect the activity and composition of microbial populations and can create better environmental conditions for the development of nonacidophilic microorganisms, resulting in increased microbial biomass and soil respiration [220,221]. Other beneficial role of liming review by Fageria and Baligar [168] include (i) reduction in solubility and leaching of heavy metals (ii) improving soil structure (iii) improving nutrient use efficiency (iv) controlling plant diseases.

Application of lime should be adequate to avoid overliming which can cause deficiencies in micronutrients like Fe, Mn, Zn Cu and B [168] and can also cause soil compaction.

- ***Application of organic waste***

To tackle soil acidity, organic waste materials are used which include; composts, manures, peats, and coal products. Several authors have reported that an increase in soil pH and decrease in aluminium saturation leading to an improvement of plant growth depends on the type of residue, its application rate and the buffering capacity of the soil [222]. During residue decomposition, there is often a transitory increase in soil pH and this induces a decrease in exchangeable and soil solution Al through their precipitation as insoluble hydroxy-Al compounds. It also confers a greater negative charge on oxide surfaces and thus tends to decrease P adsorption. The increase in pH has been attributed to a number of causes including oxidation of organic acid anions present in decomposing residues, ammonification of residue N, specific adsorption of organic molecules produced during decomposition and reduction reactions induced by anaerobiosis [223].

- ***Application of biochar***

A common consensus has been reached that the addition of biochar increases acid soil pH. As the pH of biochar in most cases is greater than 7.0, an increase of about 1.5 units higher than acid soil (normally less than 5.5) is expected upon addition of biochar [224]. This is due to their alkaline nature and high pH buffering capacity.Yuan and Xu [97] found that the increase in soil pH were more strongly correlated with biochar alkalinity ($R^2 = 0.95$) than with biochar pH ($R^2 = 0.46$). The biochar alkalinity due to the presence of carbonates and oxides react with H^+ and monomeric Al species in acid soils, thus increasing the soil pH and decreasing the exchangeable acidity [225]. In addition, it was also reported that –COO- and –O- functional groups (biochar between 300-500 °C) also contributes to acid soil remediation [86]. These functional groups can react with H^+ in the soil. Moreover, for the reduction of Al, the mechanism involves include precipitation due to reaction of Al^{3+} with alkaline materials in the biochar, complexation of Al^{3+} with organic functional groups (e.g. –COO- and –O-). Also, biochar with high surface areas and porosities are assumed to provide more adsorption sites for sorption of Al and other metals [226].

1.2.5 General conclusion on the overview of acid soil

Soil acidification in recent years has been intensified in many agricultural systems [227,228]. It is caused by the presence of acidifying parent materials, high level of acid rains, organic matter decomposition, nitrogen fertilizers input. This soil acidification leads to increase in aluminium and manganese toxicity, reduction in nutrient availability and thus crop productivity [229]. The deficiency of nutrients and the increasing availability of toxic metals can subsequently decrease soil quality and reduce crop yields. Thus the need to identify effective soil amendments to decrease soil acidification such as liming, shifting cultivation, application of slag and fly ash, application of biochar. These amendments on acid soils are crucial for sustainable agriculture development and food production.

1.3 Phosphorus in the soil

1.3.1 Brief chemistry on phosphorus

Phosphorus (P) is a naturally occurring element in the environment found in all living organisms, water and soils. It is an essential nutrient classify as a macronutrient because of it relatively large amounts required by plants. In natural system like soil and water, P exists as phosphate, a chemical form in which each P atom is surrounded by 4 oxygen (O) atoms. The simplest form of P in soil is the orthophosphate and the anionic form depends on the soil pH. In acidic soils, the orthophosphate form is primarily $H_2PO_4^-$ and in alkaline soils it is primarily $H_2PO_4^{2-}$. Below pH of 3.5, the H_3PO_4 form is predominant and above pH 11, the PO_4^{3-} is predominant. Figure 6 illustrate the pH-dependency of orthophosphate.

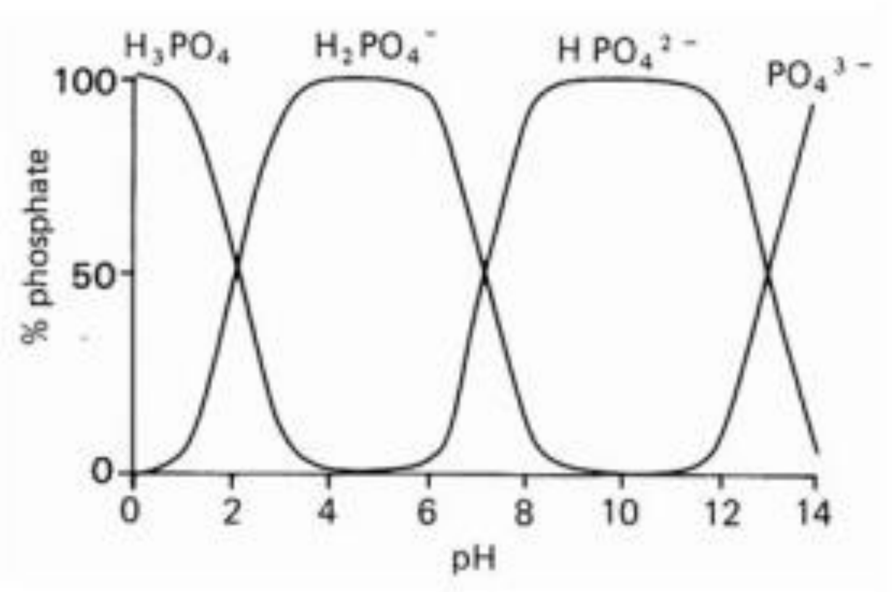


Figure 6: Distribution of phosphate species with pH

1.3.2 Forms of phosphorus present in soil and the biogeochemical cycle

- ***Forms of phosphorus***

In soil, P is found in two forms namely organic and inorganic, which makes up the total phosphorus. The main form of phosphorus in soil is the inorganic P which account to 60 – 80 % of total phosphorus [230].

P in soil exists in three different pools which differ with their availability to plants (Figure 7). They are the readily available P (solution P), the solution P (labile P) and the relatively slowly available P (non-labile P) [231]. The solution P is very small in amount and plants will only take up in orthophosphate form. The importance of solution P is due to that fact that it is the pool from which plant take P. The labile pool is P in the solid phase which is relatively easily released to the soil solution. Since solution P is small, the labile P is the main source of available P for plants. The labile pool P contain inorganic phosphate that is attached to small particles in the soil, phosphate that reacted with elements such as calcium or aluminium to form somewhat soluble solids, and organic P that is easily mineralized [232]. The non-labile pool of phosphate contain inorganic phosphate compounds that are very insoluble and organic compounds that can be mineralization by microorganism in the soil [233].

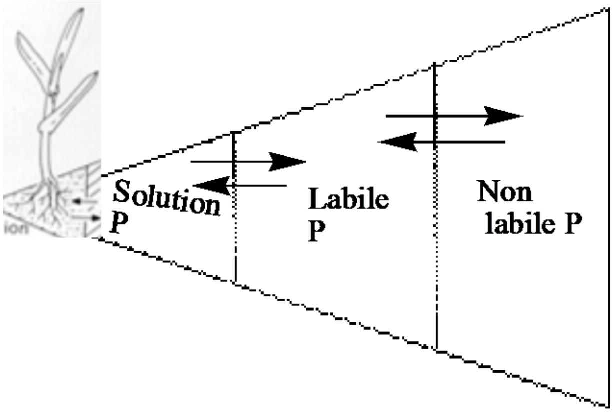


Figure 7: Phosphorus pools in the soil

- ***Biogeochemical cycle of P***

The phosphorus cycle differs markedly from the other nutrient cycles (carbon, nitrogen, and hydrogen), because phosphorus has no significant gaseous phase, and therefore, no major component to its cycle. The cycle comprises of a geological (long term) and a biological (short-term) cycle which was described by Turner and Raboy [234].

- **Geological cycle**

The geological cycle begins with the slow weathering and dissolution of phosphate minerals (mainly apatite) in the terrestrial environment. Also, P can be desorbed from clay and mineral surface. In the short term the released phosphorus is involved in the soil-plant-animal system (the terrestrial biological cycle), but in the long term it leaches slowly from the soil and is transported by rivers to the oceans. There it can be taken up by phytoplankton and then enters the aquatic biological cycle, or it can precipitate with calcium to form insoluble calcium phosphates, which are deposited onto the ocean floor. The sediments are converted to sedimentary rock by burial and diagenesis (chemical and physical changes) over millions of years, and subsequently uplifted, whereby the process begins again. The geological cycle of P is illustrated with Figure 8.

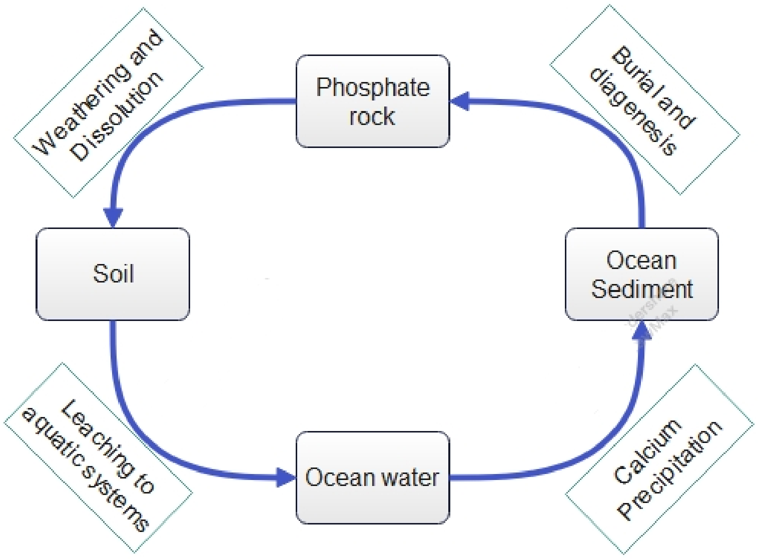


Figure 8: Simplified geological phosphorus cycle

- **Biological cycle**

Plants take up phosphorus from the soil solution as inorganic orthophosphate, but the availability of this compound in soil is typically low. In the early stages of pedogenesis (soil formation), phosphorus is released slowly by the weathering and dissolution of apatite. However, inorganic phosphorus reacts strongly in the soil, forming precipitates with calcium, iron, and aluminium, and becoming adsorbed on the reactive surfaces of clay minerals. Though precipitated, it does not mean that plants cannot access phosphorus from the soil, because as they deplete inorganic orthophosphate from the soil solution, it is replenished from the solid phase, thus maintaining relatively constant. After uptake from the soil, plants convert inorganic orthophosphate to organic forms of phosphorus such as nucleic acids and phospholipids. Therefore, phosphorus is returned to the soil in plant residues as organic phosphates. These organic compounds often represent the major soil phosphorus fraction in natural systems, so it is not surprising to find that many organisms possess complex mechanisms for accessing phosphorus from them. In particular, they are hydrolyzed by enzymes called phosphatases, released by plants and microorganisms in response to a deficiency in phosphorus. The conversion of organic phosphorus to inorganic forms (mineralization) is, therefore, a key stage in the biological phosphorus cycle. A summarised illustration of P in the soil-pant-animal system is shown with Figure 9.

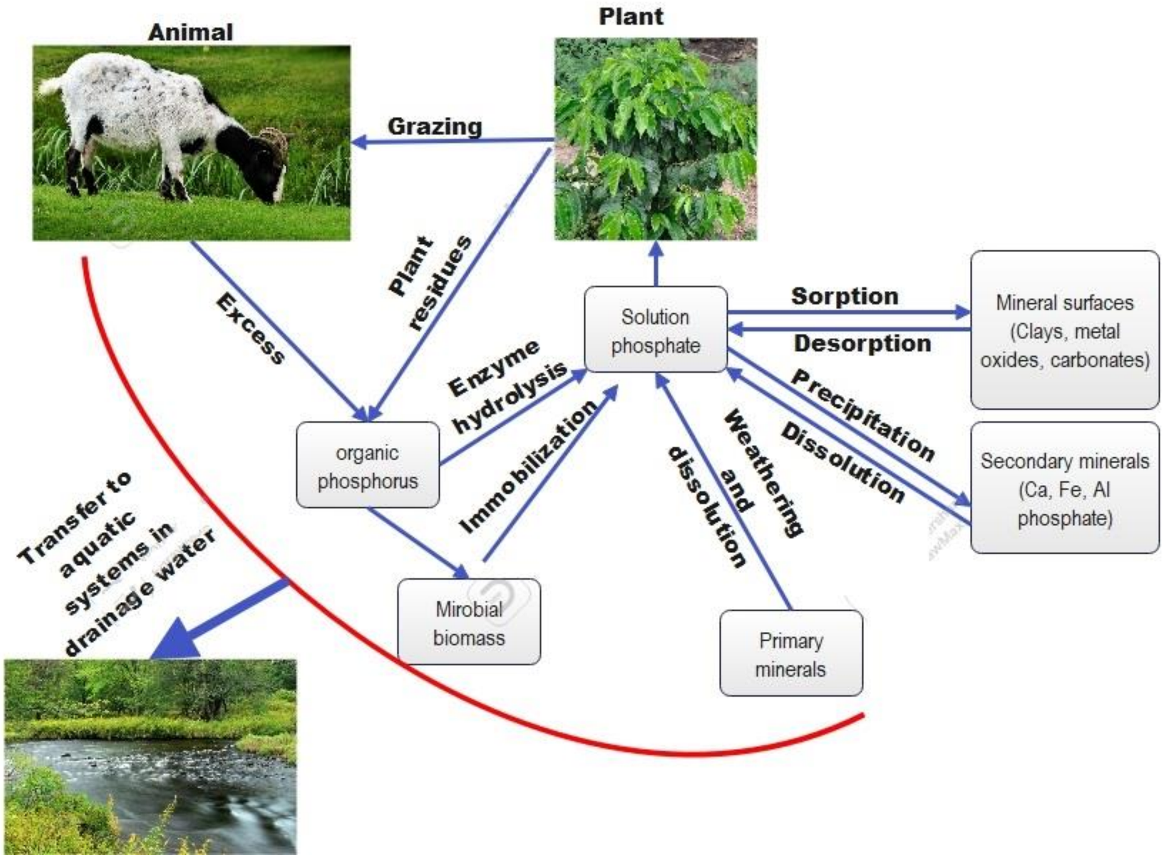


Figure 9: Phosphorus cycle in the soil-pant-animal system

1.3.3 Biological and agricultural importance of phosphorus

In modern agriculture, P is an essential element for biological systems of plants because it is part of the genetic material and the phosphate ester bond used for energy transfer reactions in organisms [235]. Phosphoproteins, enzymes and energy-rich phosphate compounds (Adenosine triphosphate) take part in reactions that control photosynthesis, respiration, protein and nucleic acid synthesis, and nutrient transport through plants cell. Phosphorus is also essential for seed production, promotion of root growth, early plant maturity, promotion of stalk length [236].

Though P benefits to agricultural system are evident, this element can be a pollutant if it moves to other site. Phosphorus transported from the soil to lakes, rivers and oceans can cause eutrophication [237]. The harmful effect of eutrophication are: depletion of oxygen which promotes conditions that convert compounds to potential toxic forms such as nitrate to ammonia, that may be harmful to aquatic animals [238]; increases the cost and difficulties in purification of drinking water; decaying pest and algae produces surface scums and undesirable odours and may also increase the population of pest and insects.

1.3.4 Phosphorus status, deficiency and availability in acidic soils

Phosphorus deficiency is a major constraint to crop production in the humid and sub-humid tropics, as most of the soils in these regions are inherently low in total P and possess a high phosphate sorption capacity resulting in extremely low availability of P [239] coupled with erosion and surface run off. In acid soils, phosphorus commonly bound with iron and aluminium through chemical precipitation or physical adsorption [171]. In West and Southern Cameroon, the evident low plant-available P is generally consistent with the low NaOH-P pool with the largest fractions due to the strong interaction with Fe/Al oxides and hydroxides [240].

Though phosphorus is highly immobile in mineral soils and causes a difficult acquisition by many plants, plants developed multiple adaptation response to P starvation. Raghothama [241] reviewed the plants multiple response to phosphate deficiency as (i) morphological response which include: Increased root:shoot ratio; changes in root morphology and architecture; increased root hair (ii) physiological response which include enhanced phosphate uptake; reduced phosphate efflux; increased phosphate use efficiency; mobilization of phosphate from the vacuole to cytoplasm; increased translocation of P within plants; retention of more phosphate in roots; secretion of organic acids; protons and chelaters; secretion of phosphatases and RNases; altered respiration; carbon metabolism; photosynthesis; nitrogen fixation; and aromatic enzyme pathways (iii) Biochemical response which include activation of enzymes; enhanced production of phosphatases; RNases and organic acids, changes in protein phosphorylation; activation of glycolytic bypass pathway, and (iv) molecular response which include activation of genes.

The availability of P to plants is controlled by physical and chemical reactions, including sorption/desorption (interactions between phosphorus in solution and soil solid phase) and precipitation/dissolution (mineral equilibra) and biological process such as immobilization (uptake by plants and microorganisms) and by mineralization (decomposition of residues) [235].

Zhu and collaborators [242] in a review classified different methods intended to accelerate and strengthen soil P transformation and availability in soil solution. They called them P activators and classified them into three types: (1) bio-inoculants and biofertilizers, including phosphate solubilizing, microorganisms and phosphatase enzymes;[178,243,244] (2) organic matter, including low molecular weight organic acids, humic acids, lignin, crop residue, manure and biochar and (3) zeolites and other materials.

The range of mechanisms involve ion the availability of P when P activators include: (1) dissolution, due to the change chemical structure of the sorbing components; (2) competitive inhibition of P sorption due to competition with phosphate for sorption sites or competition with metal oxides for exchange sites in soil; (3) organic ligands, such as carboxylic acid and phenolic hydroxyl can complex metals and release P bound to the cation; (4) enzymolysis with the catalysis of the hydrolysis of the ester-phosphate bonds, leading to the release of phosphate; (5) P release materials which contain available phosphorus which can be release into the soil.

1.3.5 Phosphorus sorption and desorption in soil

The term sorption refers to reactions namely adsorption, precipitation and diffusion into soil crystals, and it is used when the mechanism of retention at the surface is not known [245]. The mobility and fate of nutrients of plants is controled by the vital chemical process of sorption. On the other hand, desorption is the release of the adsorbate to the soil solution.

Phosphorus sorption is any mechanism whereby P is taken out of solution by soil [231]. It is used to explain chemical and physical reactions that take P from the soil solution onto the solid phase [246]. The two main types of reactions involves phosphorus sorption on the surface minerals and formation of precipitate in soil solution [247].

- ***Phosphorus sorption mechanism in acid soils***

Labile P is available for plant uptake over a relatively short time, and can be held by the soil through several possible mechanisms such as anion exchange, ligand exchange, precipitation of phosphate.

- ***Anion exchange***

Anion exchange is a simple mechanism of attraction of an anion to a positively charged surface whereby the surface charge is partly neutralized through sorption of the anion in the outer-sphere layer. P sorption by anion exchange mechanism occurs on variable charged minerals, especially Fe and Al oxides and hydroxides and 1:1 minerals such as kaolinite. This mechanism is affected by changes in soil pH [231]. As pH is greater than the point of zero charge (PZC), the surface becomes less positive and can retain less phosphorus, and then an increase in ionic strength will make the surface less positive; the opposite effect occurs if pH is less than PZC. The surface electrical potential becomes less negative at the plane of sorption by increasing the ionic strength which increases P sorption [231]. Several authors have investigated that increasing soil pH decreases surface positive charges, and this leads to decreases phosphorus sorption, thus resulting in an increase in soil solution P [248,249].

- ***Ligand exchange to Al and Fe oxides/hydroxides and edges of alumino-silicate minerals***

Phosphate adsorption on Al and Fe oxides/hydroxies and 1:1 minerals utilises a strong covalent bond due to a ligand exchange, and surface complexation, thus forming a stronger sorption mechanism as compared to anion exchange. The process takes place in two different chemical reactions which are protonation of the hydroxyl groups namely; the adsorption of phosphate due to positive electric field created and replacement of protonated hydroxyl groups with phosphate [245,250]. This leads to the formation of singly, doubly and triple coordination when hydroxyl groups are coordinated by one, two or three Fe atoms respectively. The surface reaction can be illustrated as in Figure 10.

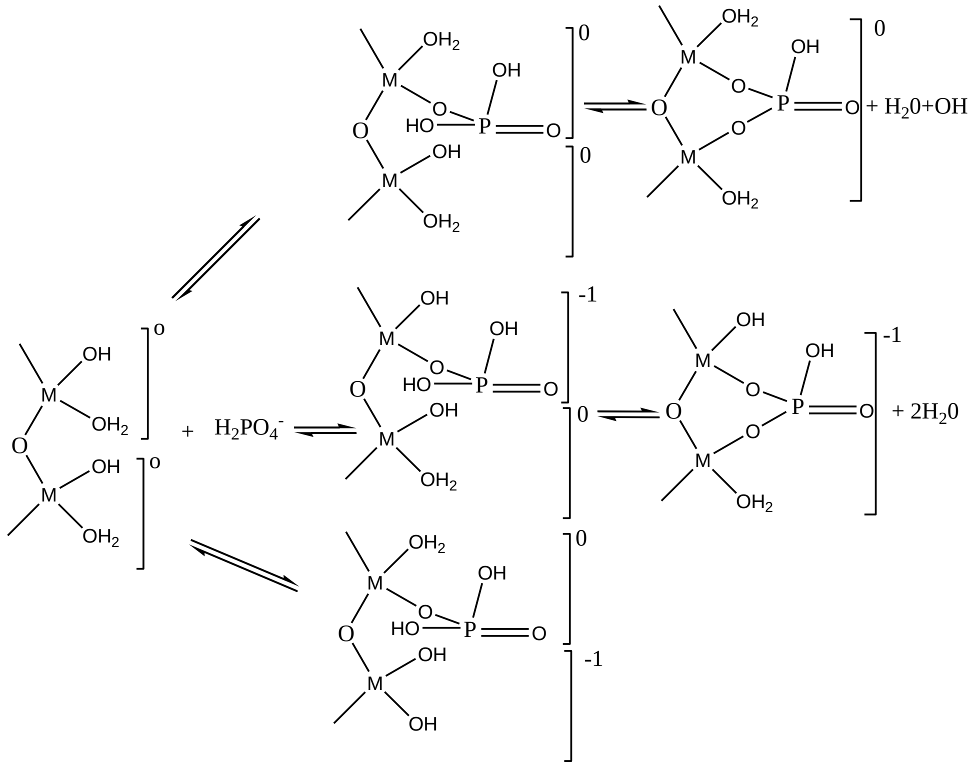


Figure 10: Changes in charge and possible changes in configuration following adsorption of the surface of a metal oxide

$$Al - OH^0 + HPO^{2-}_{4(aq)} \leftrightarrow Al - OPO_3H^- + OH^-_{(aq)} \quad (7)$$

$$Al - OH^+_2 + HPO^{2-}_{4(aq)} \leftrightarrow Al - OPO_3H^- + OH^-_{(aq)} \quad (8)$$

At low pH, the reaction is favoured, not because the surface becomes positively charge, but due to the fact that the surface functional groups possesses water molecules rather than –OH groups which are difficult to displace [251]. As pH is increased (addition of OH$^-$), the hydroxide added becomes more competitive than the phosphate onto the variable charge minerals. Thus ligand exchange of phosphate onto the surface tends to decrease.

Moreover, the ligand exchange site of P onto variable charged Al and Fe minerals can be a "point" by which begins the precipitation of Al and Fe phosphate or slow diffusion into the mineral. The process takes place by a rapid ligand exchange reaction followed by a slower surface precipitation reaction and diffusion into the interior. The diffusion of the adsorbed phosphate into the solid is termed absorption. Precipitation of Fe and Al oxides on soil mineral surface can result in the trapping of adsorbed P. The trapped P in the nanopores of Fe/Al oxides is then described as occluded thereby becoming unavailable to the plants [252].

- ***Precipitation of Al and Fe phosphate***

In acid soils, phosphate precipitates to variscite and strengite, but also into non-crystaline Al and Fe phosphate [253]. When P fertilizer is added to acid soils, there is an increase in the concentration of P in the soil solution. The excess P may precipitate into Ca, Al and Fe phosphate [254]. In soils containing minerals such kaolinite, montmorillonite, illite, goethite and gibbsite, high P solution dissolves/decomposes the soil minerals beyond releasing exchangeable cations, and precipitate Al and Fe phosphate minerals at the surface [255–258].

Decreasing the soil pH (i.e. increasing H^+), promote the dissolution of Al and Fe oxides and hydroxides through hydrolysis of Al and Fe (equation 9 and 10). The resulting soil solution of greater amount of Al^{3+} and Fe^{3+} can the directly precipitate with P, thereby removing phosphorus from soil solution.

$$Al(OH)_{3(s)} + 3H^+_{(aq)} \leftrightarrow Al^{3+}_{(aq)} + 3H_2O \tag{9}$$

$$Fe(OH)_{3(s)} + 3H^+_{(aq)} \leftrightarrow Fe^{3+}_{(aq)} + 3H_2O \tag{10}$$

- ***Precipitation of Ca phosphate***

When soil solutions become “saturated” with the Ca and P, precipitation of Ca phosphate minerals can occur. Phosphate precipitation in soil solutions includes mono-calcium phosphate, brushite and hydroxyapatite (equation 11, 12, 13 respectively).

$$Ca^{2+}_{(aq)} + 2H_2PO^-_{4(aq)} + H_2O_{(l)} \leftrightarrow Ca(H_2PO_4)_2.H_2O_{(s)}\text{(mono-calcium phosphate)} \tag{11}$$

$$Ca^{2+}_{(aq)} + H_2PO^-_{4(aq)} + 2H_2O_{(l)} \leftrightarrow CaHPO_4.2H_2O_{(s)}\text{ (brushite)} \tag{12}$$

$$5Ca^{2+}_{(aq)} + 3H_2PO^-_{4(aq)} + H_2O_{(l)} \leftrightarrow Ca_5(PO_4)_3OH_{(s)}\text{ (hydroxyapatite)} \tag{13}$$

Highly soluble Ca phosphate minerals such as mono-calcium phosphate dissolve quickly and saturate the solution with Ca and P relative to less soluble Ca phosphate minerals such as brushite and amorphous forms, allowing then to precipitate [259]. These Ca phosphate minerals slowly transform into more stable minerals (hydroxyapatite) [260]. Brushite is the predominant Ca-P phase below 6.5 [261] and above soil pH of 6.5, brushite converts to octacalcium phosphate ($Ca_8H_2(PO_4)_6.5H_20$) and hydroxyapatite [262].

The solubility of Ca phosphate depends largely on the activities of H^+ and Ca^{2+} in calcareous soil [263]. While it is often assumed that Ca phosphate only exist in high soil pH, numerous studies have identified Ca phosphate in acid soils by a variety of method [264–266]. Penn and Camberato [231] have describes several reasons for the occurrence of calcium phosphate in. First, Ca phosphate minerals may become occluded within other minerals, such as Al or Fe hydroxides, shielding them from solution. Second, increase concentration of Ca can decrease the pH required for precipitation of Calcium phosphate minerals, allowing appreciable amounts to be precipitated at pH values less than 7.

1.3.6 Phosphorus adsorption isotherms and mechanism

Adsorption isotherms can be defined as the equilibrium quantitative relationships between the amounts of adsorbed and dissolved phosphate species at constant temperatures. Phosphate sorption isotherm study is to understand the mechanism in the interaction of phosphate ions with oxides, oxyhydroxides, sesquinoxides in soil [6,267] and for evaluating the phosphate requirement of soils [268].

The precursor of the study of adsorption of phosphate in soil goes as far by in 1980 [269]. This study continues up till date with the use of sophisticated equipment with robust isotherms equations which permits to get numerous informations during the study. Some isotherm equations used Langmuir equation [270], Freundlich [271], Temkin equation [272] and Elovich equation [273]. In the literature, Langmuir and Freundlich isotherm model are the most used isotherm models used to evaluate the phosphorus requirement and the interactions of the phosphate with soil.

- ***Langmuir isotherm model***

Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has also been used to explain phosphate adsorption on soils. In Langmuir isotherm model, the following assumptions are made which defines the principle under which it is applied [274].

- There is monolayer adsorption. i.e. the adsorbed layer is one molecule in thickness.
- Localized adsorption sites, which are equivalent and identical, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites

- There is a homogenous adsorption. i.e. each molecule possesses constant enthalpies and sorption activation energy

The nonlinear form of Langmuir isotherm model used is represented by equation (14) which describes single-layer adsorption:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{14}$$

Where, Q_e (mg/kg) is the quantity of P adsorbed by the soil or soil/biochar mixture, C_e (mg/L) the quantity of P at equilibrium after adsorption, Q_{max} the P adsorption maximum for Langmuir model (mg/kg), K_L the equilibrium constant that determines the binding energy (Lkg^{-1}), the higher the K_L the stronger the binding force.

- ***Freundlich isotherm***

This is an empirical model which applies to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [275]. Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorptions process where 1/n above one is an indicative of cooperative adsorption [276]. [271] use the Freundlich isotherm for soil phosphate sorption data for twenty nine soils and found that the exponent from the isotherm thus obtained was closely related to exchangeable Al (in acid soils).

The nonlinear form of Freundlich is given in equation (15) below which describes multi-layer adsorption

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{15}$$

Where Q_e (mg/kg) is the quantity of P adsorbed by the soil or soil/biochar mixture, C_e (mg/L) the quantity of P at equilibrium after adsorption, K_F (mg/kg) the Freundlich constant indicating adsorption capacity not specifically the maximum adsorption capacity, and $\frac{1}{n}$ the adsorption intensity which indicates the heterogeneity of the material [277]

1.3.7 Phosphorus desorption

The concentration of P in the soil solution is primarily controlled by adsorption/desorption equilibria between labile Pi in the solid phase (associated with positively charged minerals such as Fe and Al oxides) defined by equilibrium concentration ratios [223]. The amount of P bound on the solid phase can result to P deficiency. The desorption of these P from the solid phase is a means of improving its amount in the soil solution.

Phosphorus desorption has been studied using water and free-P solutions such as potassium chloride and calcium chloride to induce desorption. The soil/solution ratio for the desorption process ranges from 1:10 to 1:100 and the desorption solution concentration ranges from 0.01 M to about 1 M.

- ***Phosphorus desorption mechanism in soils***

In a review published by Zhu and collaborators [242] the range of mechanism involved in the promotion of the solubilisation of insoluble inorganic P and or mineralization of organic P include (1) Dissolution. P activators change the chemical structure of the sorbing components principally via metal complexation and removal; (2) Competitive inhibition of P sorption. P activators compete with phosphate for sorption sites or compete with metal oxides for exchange sites in soil; (3) Organic ligands. Functional groups such as carboxyl and phenolic hydroxyl can complex metal ions and release P bound to these cations; (4) enzymolysis, P activators catalyze the hydrolysis of ester-phosphate bonds, leading to the release of phosphate; (5) P release. Bio-resource P activators contain both inorganic P and organic P which can be released into the soil. The phosphorus activators include (1) Phosphate solubilizing microorganisms; (2) Phosphatase enzyme and enzyme activators; (3) Low molecular weight organic acid; (4) Humic acid and lignin; (5) Crop residue and manure; (6) Biochar; (7) Zeolites and others [242].

1.3.8 General conclusion on phosphorus in acid soils

In the context of agricultural problematic soils, acid soils contain lower concentration of labile P in the soil solution. The poor concentration of P in acid soils is mostly due to is fixation to Al and Fe. Soils in South and West Cameroon are poor in available P, therefore, it is important to study the causes, propose remediation materials and procedure, and the mechanistic insight on how to improve the quantity of labile P in the soil solution. This will go a long way to improve plant growth and crop yield.

1.4 Research gaps in biochar application to acid soils in Cameroon

In Sub-Saharan Africa and especially in Cameroon, biochar faces policy, legal, institutional, technical and socio-economic barrier. To our knowledge, up to date the Cameroon government do not put much effort in the use of biochar, in putting in place clear policy or legal frameworks on biochar technologies. This can be seen in the lack of public investment in biochar while in contrast developed countries have large scale pyrolysis plants already in operation.

Currently, there is limited biochar research in institutions and universities. Up till date, available research works from institutions on biochar in the domain of agriculture include, research work done by the Institute of Agricultural Research for Development, the school of Agriculture and Environmental Sciences and in the Faculty of Science precisely in the laboratory of soil microbiology/biotechnology centre of the University of yaounde 1 [278–281]. Based on Google scholar research motor, less than 30 articles have been published on biochar as used in agriculture in Cameroon.The scientific gaps in the impact of biochar on the chemical properties of acid soils has receive less attention, and also it incorporation into soil for the sorption/desorption study is of recent. The missing knowledge in the use of biomass to produce biochar for amendments of acid soils needs to be treated.

CHAPTER 2

REAGENTS, MATERIALS AND METHODS

This section comprises of (i) reagents used in this research (ii) sampling of soil and biomass for biochar preparation and characterisation (iii) Amendments studies and chemical characterisation (iv) fixation/release studies of P on the amended soil samples and (v) the description of the statistical tools

2.1 Reagents

The reagents used for soil and biochar characterization and sorption studies are compiled in Table 2.

Table 2: List of reagents

Name	Chemical formula	Purity	Origin
1-10 Phenanthroline	$C_{12}H_8N_2$	99.9	Sigma Aldrich
Ammonium iron(II) sulphate (Mohr salt)	$(NH_4)_2Fe(SO_4)_2.6H_2O$	99.0	Prolabo
Ammonium molybdate	$(NH_4)_6Mo_7O_{24}$	99.0	Rien de Haën
Ascorbic acid	$C_6H_8O_6$	100	Prolabo
Calcium Carbonate	$CaCO_3$	99.0	Rien de Haën
Chloroform	$CHCl_3$	99.0	Prolabo
Ethanoic acid	CH_3COOH	99.8	Sharlau
Ferroin indicator	$[Fe(C_{12}H_8N_2)_3]SO_4$	/	Sigma Aldrich
Hydrochloric acid	HCl	37.0	Sharlau
Hydrogen peroxide	H_2O_2	/	Sigma Aldrich
Hydroxylamine	NH_2OH	99.0	Sigma Aldrich
Potassium antimonyl tartrate	$K_2Sb_2C_8H_4O_{12}\cdot 3H_2O$	99.0	Sigma Aldrich
Potassium chloride	KCl	100	Prolabo
Potassium dichromate	$K_2Cr_2O_7$	99	PubChem
Potassium fluoride	KF	99.0	Rien de Haën
Potassium hydrogen phosphate	KH_2PO_4	99.5	Prolabo
Sodium acetate	$NaOOCCH_3$	99.0	Synth
Sodium Hexametaphosphate	$Na_6(PO_3)_6$	/	/
Sodium hydrogen carbonate	$NaHCO_3$	99.7	Prolabo
Sodium hydroxide	$NaOH$	98.0	Sharlau
Sodium Nitrate	$NaNO_3$	98.0	Prolabo
Sulphamic acid	NH_2SO_3H	99.3	Sigma Aldrich
Sulphuric acid	H_2SO_4	95.0	Prolabo

2.2 Sampling of soil and biochar, biochar preparation

2.2.1 Sampling site description

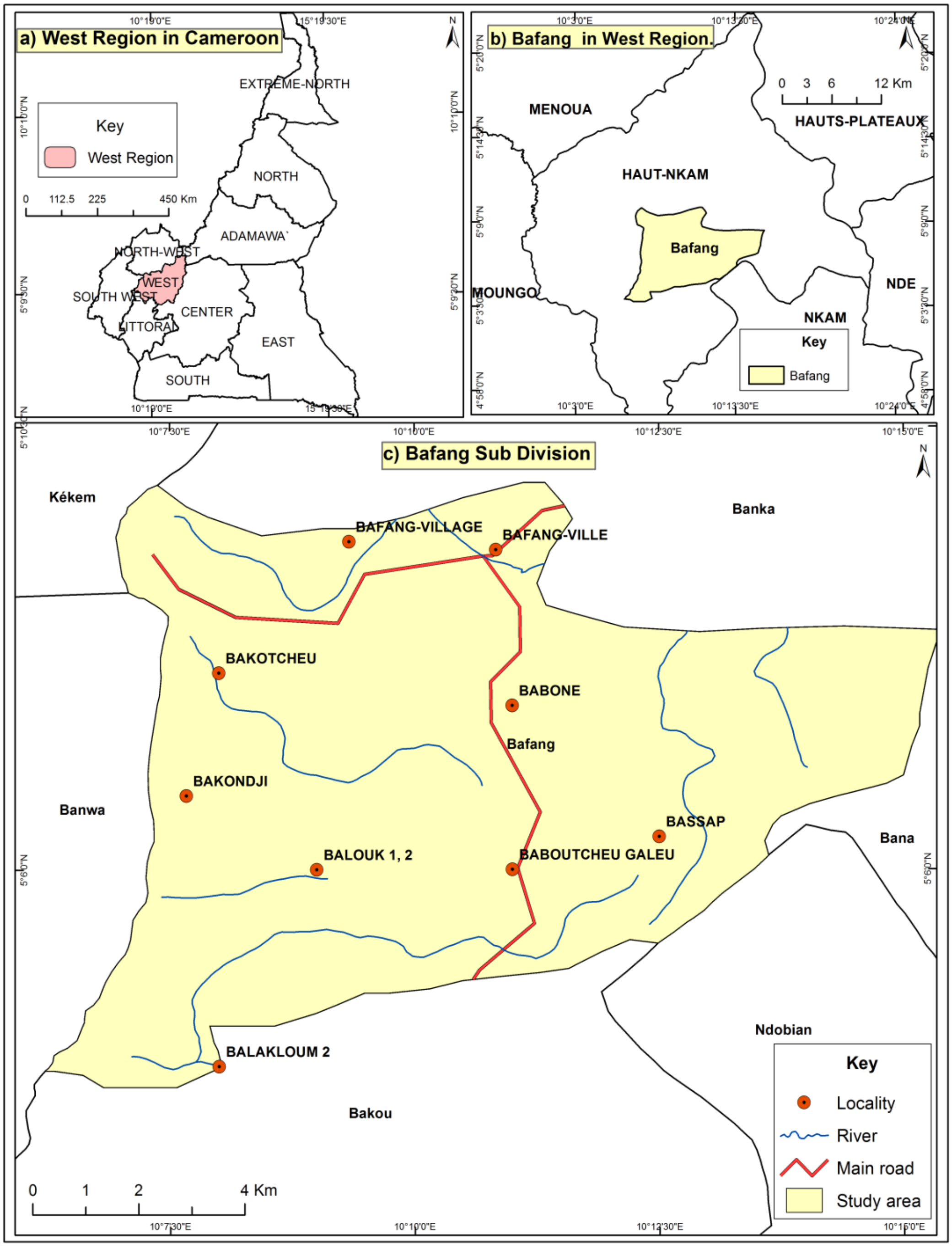


Figure 11: Location of Bafang subdivision

On the administrative point of view, Bafang village is found in Bafang subdivision which is located in the Upper-Nkam division, West region of the Republic of Cameroon. The subdivision comprises of the following villages Bafang, Babone, Baboutcheu-Ngaleu, Baboutcheu-Nitcheu, Bankondji and Bassap.

Soils in Bafang are mostly ferrallitic, humus-bearing and hydromorphic, and formed on volcanic, plutonic and metamorphic formations including basalts, granites, mylonites and gneisses [282]. The topography surrounding Bafang shows very large variations in altitude, with a variation in altitude of maximum 407 meters and an average altitude above sea level of 1197 meters and geographically located at coordinates (sample zone) 5°08’55” N and 10°09’32” E and 1128 m altitude. In Bafang, the rainy season is oppressive and overcast, the dry season is wet and cloudy overall and the climate is warm throughout the year with an average rainfall of 14 mm. During the year, the temperature generally ranges from 14°C to 28°C. Bafang is covered by trees (37%), bushes (34 %) and cropland (23%) [283].

3.2.2 Soil sampling

Topsoil samples were collected randomly on a 2 hectare mixed cocoa and coffee farm in Bafang, West region of Cameroon. Before digging and sampling at a particular point, the vegetative cover was cleared with a cutlass and the soils were sampled using a shovel from a plough depth of 15 cm. The soil samples were brought to the laboratory, air-dried, crushed, sieved through a 2 mm sieve to remove twigs, and plant roots and stored in plastic bags for physicochemical analyses and incubation studies.

3.2.3 Biochar sampling

Coffee husks and cocoa pod husk were collected from coffee processing factories and cocoa farms respectively, located in Bafang, West region of the Republic of Cameroon. These biomasses were dried and ground to pass through a 1.0 mm sieve to ensure uniformity of samples during pyrolysis and then dried at 105°C. They were stored in plastic bags for biochar production.

3.2.4 Biochar preparation

The two biomasses were placed in a ceramic crucible, and then covered with a fitting ceramic lid. The ceramic crucibles were placed in a muffle furnace and the biomasses pyrolysed under oxygen-limited conditions at two different temperatures (350 °C and 550°C). The pyrolysis rate temperature was set at 10°C/min and held constant for 4h. After 4 h, the biochar samples were left to cool in the muffle furnace to room temperature; it was then ground to very fine particles. For each pyrolysis process, the crucible containing the biomass or the biochar was weighed and from which the biochar yields were calculated using equation 19.

$$biochar\ yield\ (\%) = \left[\frac{m_f}{m_o}\right] x\ 100 \qquad (19)$$

Where m_f is the dry mass (g) of the produced biochar and m_o is the dry mass (g) of the biomass.

The biochars were hereby referred to their biomass abbreviation and pyrolysis temperature, i.e. biochar from coffee husk produced at 350 and 550 was represented as CH350 and CH550 respectively. Same for coffee husk pod and it biochars produced at the same temperatures as the latter being represented as CP350 and CP550 respectively. Biochar samples were kept in polythene bags for characterization and incubation studies.

2.3 Soil and biochar characterization

2.3.1 Soil characterisation

- ***Bulk density***

The bulk density is used to measure the soil compaction. It depends on the organic matter present in the soil, soil texture, density of soil minerals and their packing arrangement [284]. The bulk density of the soil, was determined using the core sample method of [285]. Prior to collecting the soil sample for bulk density determination, prepare an undisturbed flat horizontal surface with a spade. Using a harmer, a cylindrical steel ring is push gently into the soil, then excavate around the ring without loosening the soil. With the aid of a knife, the ends of the cylindrical steel were levelled and capped at both ends. The samples were poured in an envelope, seal and labelled appropriately.

In the laboratory, the samples were emptied onto clean dry can and mass measured and recorded as m_1. The cans with soil samples were placed in an oven and dried for 72 h at 105 °C and the mass was taken after cooling in a desiccator and recorded as m_2. Using equation (20), the bulk density was calculated

$$Bulk\ density\ \left(\rho_{(gcm^{-3})}\right) = \frac{m_2 - m_1}{V} \qquad (20)$$

Where

m_1 = mass in kg taken after oven drying the moisture can and its contents.

m_2= mass in kg of can and moist soil

V = volume of soil, which is determine by calculating the volume of the cylindrical steel ring ($\pi \frac{d^2}{4} h$, with d as the diameter of the ring and h the height, all in metres).

From the methodology of the determination of bulk density, the data obtained can be used to determine the soil water content of the soil (equation 21) and the soil porosity (equation 22).

$$soil\ water\ content\ (g/g) = \frac{m_2 - m_1}{m_1} \qquad (21)$$

$$soil\ porosity(\%) = 1 - \left(\frac{Bulk\ density}{particle\ density}\right) \times 100 \qquad (22)$$

Where the particle density of the soil was determine to 2.0 g/cm^3

- ***Soil particle size distribution***

The particle size distribution of the soil was determined by the pipette method described by Sakar and Haldar [286]. The method is based on the principle of dispersion and sedimentation techniques (following stokes law) employed to a given weight of soil samples. 50 g of fine soil texture sieve to less than 2 mm was weighed and placed into a 250 mL beaker and 50 mL of 5 % H_2O_2 was added. The beaker was placed in a water bath until oxidation of organic matter was complete; the beaker was removed and cold. The content of the beaker was transfer into a dispersing cup containing 500 mL of deionised water and 100 mL of 5% Sodium Hexametaphosphate (Calgon) solution was added. The suspension was agitated at 180 rpm using an electric stirrer for 3 h. The suspension was then transferred into a 1 L measuring cylinder and deionised water added to the 1 L mark.

The mouth of the cylinder was closed with a stopper and shaken vigorously upside down and back several times and placed on the table and time noted. Five minutes later, clay and silt particles were soaked out by lowering the pipette in the cylinder at a depth of 10 cm from the top and carefully soak out the liquid. The pipette was emptied in a dry can and evaporated to dry at maximum temperature of 105 °C. The second sampling is done after 8 h for clay particles alone.

To determine the sand content, the suspension were washed thoroughly with distil water until the supernatant was clear. The suspension was poured into a moisture can with a known weight and oven dried at 105 °C. The weight of the sand was measured using an electronic balance. The percentage particle size distribution for the soil samples were then computed as follows:

$$\% \, Clay = \frac{mass\ of\ solid\ obtain\ after\ 8\ h}{mass\ of\ soil\ sample} \times 100 \qquad (23)$$

$$\% \, Silt = \frac{mass\ of\ soild\ obtain\ qfter\ 5\ min - mass\ of\ solid\ obtain\ after\ 8\ h}{mass\ of\ soil\ sample} \times 100 \qquad (24)$$

$$\% \, Sand = \frac{mass\ of\ rest\ solid\ in\ the\ cylinder}{mass\ of\ soil\ sample} \times 100 \qquad (25)$$

The result obtain was inserted in the online soil texture calculator [287] to get the soil texture.

- ***Soil pH***

In soil science, the pH characterizes the physicochemical environment of a soil at a given site, this being the result of instantaneous equilibrium controlled by different components of the medium. Soil pH measurement is classified in four main types: (1) On aqueous suspensions soils; (2) on saturated pastes; (3) on extracts of saturation; and (4) “In situ” measurements. In this study, the measurement on aqueous soil suspension was used.

In practice, 10 g of a 2 mm sieve soil was weighed and introduce in 25 mL of deionized water (ratio soil:water 1: 2.5) found in a 100 mL centrifuge tube. The mixture was shaking for 1 h on an end-to-end table shaker oscillating at 150 rpm and then left to stand for 30 min. The electrode pH meter (HANNA Instruments) was immersed in the supernatant taking care that the bulb is submerged. The value of the pH was read on the screen of the pH meter [82].

- ***Soil electrical conductivity***

Soil electrical conductivity is the measure of the amount of salts (total concentration of anions and cations) in soil and it is widely used for soil salinity test [288]. It is based on the principle that solutions with a higher concentration of salts have a greater ability to conduct electrical current. Electrical conductivity of soils is usually carried out on the saturated or diluted extract, but sometimes directly on the saturated paste itself. In this work, electrical conductivity was measured on the saturated extract obtain from shaking soil in deionized water in the ratio 1: 5.

In practice, 10 g of a 2 mm sieve soil was weigh and introduce in 50 mL of deionized water (ratio soil:water 1:5) found in a 100 mL centrifuge tube. The mixture was shaking for 1 h on an end-to-end table shaker oscillating at 150 rpm and left to stand for 30 min. The electrode electrical conductivity meter (WTW Multi 340i) was immersed in the supernatant and the value read [82].

- ***Available phosphorus (Olsen P)***

Over the past years, several chemical extractants have been developed from the concept of simulating plant root activity and with the purpose to obtain an appropriate measure of the readily soluble inorganic forms to represent the plant available soil P. The most common methods along with extractant composition, soil:extraction ratio and shaking time are presented by Sakar and Haldar [286]. Some methods include: Morgan's method, Mehlich's method, Bray's 1 method, Bray's 2 methods, Troug's method and Olsen's method.

In this research work, the Olsen method was used because of its high correlation of soil test with crop response and it works for all types of soil including acid, neutral, alkaline and calcareous. Olsen's method uses the Olsen extraction solution made of 0.5 M $NaHCO_3$ at pH 8.5. This solution is commonly called the Olsen reagent. The extraction process is done using the soil/Olsen reagent ratio 1:20 and shaking for 30 min on an oscillating table [289]. The mixture is centrifuged and then filtered. Then an aliquot is taken for P spectrocolorimetry determination using [290].

- ***Exchangeable acidity and Exchangeable aluminium***

Measurement of exchangeable acidity is useful in soil sciences especially in agronomy to determine aluminium phytotoxicity. In acid soils, the exchangeable acidic cations are H^+ and Al^{3+} which constitutes the exchangeable acidity while Al^{3+} constitutes the exchangeable Aluminium.

The determination of exchangeable acidity, aluminium, is based on the principle of sample washing with a saline solution of 1 M KCl solution proposed by Pansu and Gautheyrou [82]. The solution extract was obtained by mixing 5 g of soil samples with 30 mL of 1 M KCl solution in an agitation tube and shaking for 1h. The supernatant was filtered and later 10 mL of 1 M KCl was re-added to the samples in the agitation tube for the second washing process and shaking for 10 min then filtered. Then 5 ml of the saline solution was added to the residue for rinsing. The shaking speed was maintained at 200 rpm. The total volume of the extract was maintained was then adjusted to 50 mL.

Measurement of exchangeable acidity

For the determination of exchangeable acidity, 25 mL of the extract was put in a conical flask and three drops of phenolphthalein solution added. It was then, titrated against 0.01 M NaOH until the mixture turns pale pink. A blank titration was also done. Then, the extracts were kept to measure exchangeable aluminium. The volume of NaOH was recorded at end point. The reaction in the conical flask can be described with equation (26) and (27).

$$\mathrm{H^+_{(aq)} + OH^+_{(aq)} \rightarrow H_2O_{(aq)}} \tag{26}$$

$$\mathrm{Al^{3+}_{(aq)} + 3OH^+_{(aq)} \rightarrow Al(OH)_{3(aq)}} \tag{27}$$

Using equation (28), the amount of exchangeable acidity can be calculated.

$$\text{Exchangeable acidity } [\mathrm{cmol(H^+)kg^{-1}}] = \frac{100\times(\mathrm{V_1 - V_b})\times \mathrm{M} \times \mathrm{A}}{\mathrm{w}} \tag{28}$$

Where, $V_1(mL)$ is the volume of NaOH at end point, V_b (mL) is the volume of NaOH used for blank titration, M is the molarity of NaOH, A is the aliquot factor (A= 2) and w is the mass of air-dry soil (kg).

Measurement of exchangeable aluminium

For Exchangeable Al, the 25 mL extract used to measure exchangeable acidity was used. To it, drops of 0.01 M HCl is added to destroy the pale pink colour. Then 5 mL of 1 M KF was added. If the the colour of the solution changes to pink, it indicates the presence of Al^{3+} released from $Al(OH)_3$ base on equation (29)

$$Al(OH)_{3(s)} + 6KF_{(aq)} \rightarrow K_3AlF_{6(aq)} + 3KOH_{(aq)} \tag{29}$$

The pink extract was titrated with 0.01 M HCl until the discoloration of the solution. The volume of HCl recorded at endpoint was used to calculate the amount of exchangeable aluminium. The blank samples were treated in the same way. The amount of exchangeable Al was calculated using equation (30).

$$\text{Exchangeable Al }(\text{cmolkg}^{-1}) = \frac{100 \times V_2 \times A}{w} \tag{30}$$

Where $V_2(mL)$ correspond to the volume of HCl at endpoint, A is the aliquot factor (A=2) and w is the mass of air-dry soil (kg).

- ***Exchangeable Iron***

Exchangeable Fe was determined by analyzing an aliquot of the extracted solution through the complexation of the Fe^{2+} present with ortho-phenanthroline and the amount read with visible-spectrometer at maximum wavelength of 510 nm.

2.3.2 Biochar characterisation

- ***Biochar pH***

The importance of biochar pH is due to its influence on soil pH and soil acidity. To determine biochar pH, various experimental conditions are used, such as biochar: water ratio (1:5, 1:10 and 1:20), equilibration time (1 h, 2 h, 24 h), and at times the used of salt solution ($CaCl_2$ or KCl) [76].

The recommended method proposed by Singh and collaborators [291] is used in this work. In practice, five grams of biochar were mixed with 50 mL of deionized water in a centrifuge tube and shaking on a head-on agitating table at 200 rpm for 1 h. The mixture was left to stand for 30 min then the pH probe dipped gently in the supernatant and the pH read. All experiments were done in replicates.

- ***Biochar electrical conductivity***

The amount of soluble salt in a biochar solution is important since high rates of biochar application to soil may adversely affect salt sensitive plants [20].The ratio of the biochar to water in the suspension affects the electrical conductivity values. In this work the recommended method proposed by Singh and collaborators [291] was used.

In practice, five grams of biochar were mixed with 50 mL of deionized water in a centrifuge tube and shaking on an end-to-end agitating table at 200 rpm for 1 h. The mixture was left to stand for 30 min then the electrical conductor probe dipped gently in the supernatant and the electrical conductivity read. All experiments were done in replicates.

- ***Ash content***

The purpose for the determination of the ash content is to evaluate the alkaline nature of the biochar. Ash content was determined by dry combustion in a muffle furnace at 750 °C for 6h [28]. 2 g of oven-dried biochar was introduced in a pre-weighed ceramic crucible then placed in a muffle furnace and heated at 750° C for 6 h. After cooling, the remaining solid (ash) was weighed. The percentage of ash content was calculated using equation (31):

$$\text{Ash content}(\%) = \left[\frac{\text{remaining solid wt(g)}}{\text{Biochar wt (g)}}\right] \times 100 \tag{31}$$

- ***Acid-base titration curve to evaluate biochar alkalinity***

The alkalinity of the biochar samples was determined from the biochar pH titration curve proposed by Yuan and co-workers [86]. Summarily, 0.5g of the biochar samples were placed in a 50 mL beaker, followed by 20 mL of deionized water, and stirred with a magnetic stirrer for 2 h at room temperature. The mixture was centrifuged and 15 mL of the supernatant was collected and titrated by incremental amount of 0.1 M HCl till the endpoint of the supernatant reads pH 2.0.

The data obtain was used to plot a graph of pH versus volume of HCl from which the amount of HCl consume at pH 7 and 2 was recorded for the determination of biochar alkalinity at this pH. The biochar alkalinity was determine using equation (32)

$$\text{Biochar alkalinity} = \frac{\mathrm{n_{HCl(s)}} - \mathrm{n_{HCl(b)}}}{\mathrm{m_b}} \tag{32}$$

Where $n_{HCl(s)}$ is the amount of HCl consume by the biochar sample at the given pH, $n_{HCl(b)}$ is the amount of HCl consume by the blank solution, and m_b is the oven-dry mass of biochar samples

- ***Acid-neutralising capacity***

The Acid-neutralizing capacity of biochar was determined by mixing biochar in a solution of HCl and back titrating with NaOH [292]. Concretely, 0.5 g of biochar samples was added to 50 mL of a solution of 0.05 M HCl and 0.1M $NaNO_3$. The mixture was agitated on a head-on agitating table for 16 h. The mixture was filtered through a filter paper and the filtrate back titrated with a solution of 0.05 M NaOH and 0.1 M $NaNO_3$ solution. The acid-neutralizing capacity express in cmol(H^+)/kg was calculated using equation (33).

$$\text{Acid} - \text{neutralising capacity } (\text{cmol}(\text{H}^+)/\text{kg}) = \frac{100 \times (\text{V}_\text{b} - \text{V}) \times \text{M} \times \text{A}}{\text{m}} \tag{33}$$

Where V_b is the volume in mL of NaOH used for blank titration, $V$is the volume in mL of NaOH used for filtrate titration, $M$is the concentration of NaOH, A is the aliquot factor (2), and m is the mass of biochar in kg.

- ***$CaCO_3$ equivalence***

The determination of $CaCO_3$ equivalence gives an indication of the biochar liming potential. $CaCO_3$ equivalence was determined following the method proposed by Rayment and Lyons [88]. Briefly, 10 mL of 1 M HCl solution was added to 0.5 g of biochar sample, and then shaken for 2 h and left to stand overnight. The slurry was then titrated with 0.5 M NaOH until pH 7. A reference sample of $CaCO_3$ powder (previously dried at 105 °C for 1h) was included in the batch. Liming equivalence was calculated using the equations (34) and (35).

$$\text{CaCO}_{3(\text{s})} + 2\text{HCl}_{(\text{aq})} \rightarrow \text{CaCl}_{2(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} + \text{CO}_{2(\text{g})} \tag{34}$$

$$\text{CaCO}_3\text{equivalent}(\%) = \frac{\text{M} \times (\text{a} - \text{b}) \times 10^{-3} \times 100.09 \times 100}{2 \times \text{W}} \tag{35}$$

Where M is the molarity of NaOH ($moll^{-1}$); a is the volume of NaOH being used (mL) for the blank; b is the volume of NaOH being used (mL) for the biochar sample; 10^{-3} is to convert the volume from mL to L; 100.09 is the molar mass of $CaCO_3$; 100 is the multiplier for obtaining % $CaCO_3$ equivalent; W is the mass of biochar (g); 2 is one mole of $CaCO_3$ consumes two moles of HCl in the chemical reaction.

- ***Available phosphorus***

Initially developed for calcareous soils, it is suitable for a wider range of soils and can be adapted for biochar. The Olsen extraction solution consists of $NaHCO_3$ at 0.5 mol/L buffered at pH 8.5 with NaOH. The extraction process was done using biochar-Olsen solution ratio 1:20, agitating for 30 min on an oscillating table [289]. The mixture was centrifuged and filtered. Then an aliquot was taken for P spectrocolorimetry (maximum wavelength of 889 nm) determination using the Murphy and Riley [290] method.

- ***Total organic carbon and organic matter content***

The wet oxidation method proposed by Walkley and Black [293] was used, in which the Organic carbon is oxidized by potassium dichromate with sulphuric acid without external heating.

Concretely, 0.05 g of biochar samples oven dry and grind to pass through a 0.2 mm sieve was placed in 250 mL conical flask, and 10 mL of 0.083 M of potassium dichromate solution was added. Then, 2.5 mL of concentrated sulphuric acid was added gently and left for stirring for 5 min on a magnetic stirrer. The mixture was left to stand for 1 h for further oxidation and cooling of the mixture. Thereafter, 2 g of Potassium fluoride was added plus 1 mL of Ferroin indicator. The Organic carbon content after the oxidation reaction was determining by titration of the left over potassium dichromate using 0.125 M of Mohr salt (ammonium iron(II) sulphate) solution. The blank experiment was also done with the absence of the samples. These experiments were performed in triplicates. The organic carbon content was determined using equation (36).

$$\text{Organic carbon (g/kg)} = \frac{(V_b - V_s) \times C_{Fe^{2+}} \times 0.003 \times 1000}{M} \quad (36)$$

Where V_b is the volume of Mohr's salt solution used for titration of the samples, V_s the volume for titration of blank sample in litres; $C_{Fe^{2+}}$ is the molarity in mol/L of the Mohr's salt solution; 0.003 gmmol^{-1} represents the ratio $[(0.012)/4]$, where 0.012 is the molecular mass of C (gmmol^{-1}, and 4 refers to the number of electrons involve in the oxidation of Organic carbon and M the mass of biochar in grams

Total organic carbon was calculated by applying the recovery factor of 0.77, thus given by equation (37).

$$\text{Total organic carbon (g/kg)} = \frac{(V_b - V_s) \times C_{Fe^{2+}} \times 0.003 \times 1000}{M \times 0.77} \quad (37)$$

Considering that carbon in organic matter of soils is of average 58%, a conversion factor of 1.724 was used to estimate the quantity of organic matter from the quantity of total organic carbon in the biochar. Equation (38) was used to estimate the quantity of organic matter:

$$\text{organic matter (g/kg)} = \text{Total organic matter(g/kg)} \times 1.724 \quad (38)$$

- ***Fourier Transform Infra-red (FTIR) analysis***

Infra-red spectroscopy is a class of spectroscopy that deals with the infra-red region of the electromagnetic spectrum. The FTIR is based on the absorption of infra-red radiation by the analysed material. It enables the analysis of infra-red radiation absorption bands to identify chemical functions present in a material. This technique can be used for the identification of compounds [294].

In this work, FTIR analyses were performed in the Analytical Chemistry laboratory of the University of Yaounde 1 on an Alpha spectrometer from Bruker Optics. Few milligrams of biochar samples were mixed with spectroscopic grade KBr; the mixture was ground in a clean mortar. The ground mixture was pressed into an Al holder for analysis. The scans were obtained in the range from 400 to 4000 cm^{-1}.

- ***X-ray diffraction analysis***

X-ray diffraction (XRD) analysis of biochar helps in the identification of crystalline materials which may be useful in predicting the biological availability and release to soil solution essential, non-essential and toxic elements in biochar-amended soils. Mineralogical analysis of biochar can also identify mineral impurities in biochar that might have originated from contaminated feedstock in the process of making of biochar. X-ray diffraction is a non-destructive technique that is widely used to identify crystals in a mixture with other crystalline or amorphous phases.

The XRD characterization of the biochar samples was done in the Univerität Hannover at the institut Für Mineralogie, Leibniz, Hannover Germany. The XRD patterns of the prepared biochar were registered with CuKα radiation between 5 and 80° (2θ) for 7 h in steps of 0.03° using Bruker D4 X-ray diffractometer.

- ***Scanning electron microscope-energy dispersive spectroscopy analysis***

Scanning Electron Microscope (SEM) is a type of electron microscope that scans surfaces of materials that use a beam of electrons moving at low energy to focus and scan samples. It has been a common and often indispensable tool in the characterization of the structures of a wide range of materials and biological specimens. The technique has been in widespread use for around 50 years and is now very mature and well understood. **Energy dispersive analysis spectroscopy (EDS)**, gives both qualitative and quantitative analysis, of a sample, including what elements type is present, their percentages and distribution concentration within the sample [295].

The SEM-EDS analysis of the biochar samples was performed in the Indiana University of Pennsylvania at the kopchich college of Natural Science and mathematics. The analysis was done as follow: first, the samples were placed in liquid nitrogen for approximately 2 minutes. Then, the samples were coated with 10 nm gold layer using the rotatory pump sputter coater (Leica EM ACE600, Wetzaler, Germany). The coated samples were loaded on the

ThermoScientific Prisma E SEM with an Oxford EDS system for SEM-EDS. These observations were operated at an accelerated potential of 20.00 KeV and magnifications of SEM images at magnification 500X, 1000X 1500X, 2000X and 3500X taken. On selected spots on the samples, the beam of electrons is stationary held for the acquisition of EDS spectrum and the percentage composition of elements determine using incorporated software.

2.4 Soil amendments studies and characterization

2.4.1 Soil amendments

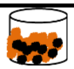
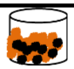
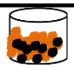
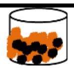
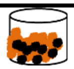
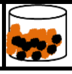
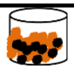
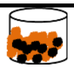
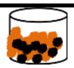
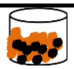
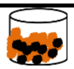
- ***Incubation studies and experimental design***

Coffee husk and cocoa pod husk biochar at two pyrolysis temperature i.e. 350 °C and 550 °C were used for the incubation studies to assess the changes in the physico-chemical properties of the acid soil samples and the effect of P sorption in the amended acid soil.

In the laboratory, transparent incubation plastic pots were filled with 100 g of soil. Biochar were added at amendment rate of 0 g/kg, 20 g/kg, 40 g/kg, and 80 g/kg and then thoroughly homogenized. The amended and unamended soil samples were wetted with deionized water at 70 % field water holding capacity of the soil and then incubated for 7, 14, 30, 45, and 60 days. The pots were covered with lids having small holes on them to prevent the rapid evaporation of soil moisture and permit the passage of air. All treatments were done in quadruples and left at room temperature. Every three days, water was added to maintain constant moisture content throughout the experiment. At the end of incubation periods, the amended and unamended soil samples were ground and sieve to < 2 mm and then store back in their incubation plastic cups.

The study was set-up in the Laboratory of analytical chemistry of the University of Yaounde 1. Table 3 shows the combination of soil treatments consisting of biochar types, amendment rate, and incubation days. After incubation, the soil-biochar mixture was labelled as SCH350, SCH550, SCP350 and SCP550 for the main 4 classes of the soil-biochar mixture.

Table 3: Combination of soil treatments (biochar types, amendment rate, and incubation days)

Biochar type	**CH350**				**CH550**			
AR ID	0	20	40	80	0	20	40	80
7								
14								
30								
45								
60								
Biochar type	**CP350**				**CP550**			
AR ID	0	20	40	80	0	20	40	80
7								
14								
30								
45								
60								

2.4.2 Characterisation of amended soils

- ***Soil-biochar mixture pH and EC***

The amended soil pH was determined by mixing soil and deionized water in the ratio 1:2.5 (10 g of soil in 25mL of water) while soil electrical conductivity was determined by mixing soil and water in the ratio 1:5 (10 g of soil in 50 mL of water). The mixture was shaken for 1h on an oscillating table at 150 rpm and left to stand for 30 min. The pH metric and conductimetric were introduced into the supernatant of their respective solutions [82].

- ***Exchangeable acidity, Aluminium and Iron***

The determination of exchangeable acidity, aluminium, and Iron is based on the principle of sample washing with a saline solution of 1 M KCl solution based on the method proposed by Pansu and Gautheyrou [82] as described in section 3.3 sub-section 3.3.1.

- ***Available phosphorus***

Available P was determined using the Olsen reagent (0.5 M $NaHCO_3$ pH 8.5). Briefly, the extraction procedure was done by mixing soil/soil-biochar with Olsen reagent in the ratio 1:20, then agitate for 30 min on an oscillating table [289]. The mixture was then centrifuged and filtered. Then an aliquot was taken for P spectrocolorimetry analysis using the Murphy and Riley procedure [290].

- ***Total organic carbon and organic matter content***

Walkley and Black [293] Procedure was used for the quantification of soil organic carbon from soil and Soil-biochar mixture. Concretely 1 g of amended and unamended soil samples was placed in a 250 mL conical flask and then 10 mL of 0.167 M of $K_2Cr_2O_7$ was added followed by an adequate volume of concentrated H_2SO_4. The mixture was stir for 10 mins and then left to cool. Prior to titration against 0.5 M of Fe^{2+}, potassium fluoride followed by 1 mL of ferroin solutions were added. The volume of Fe^{2+} obtain at the end of titration is used to determine the soil organic carbon content. The calculations involve in the determination of total organic carbon and organic matter content is found in section 3.3 of sub-section 3.3.2.

- ***Point of net zero charge***

The point of zero charge of a material is the pH of the solution at which the surface of the material has a net neutral charge. This pH is generally noted pH_{PZC}. This characteristic is particularly interesting when the sample has chemical functions whose charges may vary with the pH of the solution. Functional groups such –OH, COOH, COOC, $-NH_2$ in clay of soils and biochar is susceptible to interact with hydrogen ions in solution. Three cases can be presented depending on the value of the pH of the solution:

- $pH < pH_{PZC}$; the material has an overall positive charge;
- $pH = pH_{PZC}$; the material is overall neutral;
- $pH > pH_{PZC}$; the material has an overall negative charge.

In the presence of charged species, we can observe an electrostatic repulsion or an electrostatic attraction between the charged ions and the material depending on the pH of the solution. This phenomenon can therefore lead to an amelioration or decline of the adsorption properties of the material.

In this work, the salt addition method was used for the determination of the PZC [296]. In practice, 0.2 g of soil and soil-biochar mixture was added to a series of 25 mL tubes containing 15 mL of 0.05 M $NaNO_3$ solution whose pH (pH_i) was adjusted in the range 2, 3, 4, 5, 6, 7, 8, 9, and 10 with 0.1 M HNO_3 and 0.1 M NaOH. The tubes were agitated for 24 h on a head-on agitator at 200 rpm, then left to settle. The pH (pH_f) of the supernatant in each tube was then measured. The PZC were obtained after plotting a graph of pH_f-pH_i against pH_i, i.e. at the pH at which the curves cuts the pH_i axis.

2.5 Phosphorus fixation studies experiment

2.5.1 Phosphorus adsorption experiment

To determine sorption characteristics, related to soil-biochar properties and elucidate the mechanisms involved, sorption experiments were performed. For this study, selected samples were soil and soil-biochar mixture amended at the rate of 0, 20, 40 and 80 gkg^{-1} and incubated for 7 and 60 days. The choice of these two different length days of incubation was due to the significant change in their physic-chemical properties.

In practice, 0.2 g of each sample was mixed with 10 mL of KH_2PO_4 solution containing 0, 5, 10, 20, 80, 160, 320 and 480 mg/L P and 0.01 M KCl as background electrolyte in 25 mL centrifuge tubes. Then two drops of chloroform was added in each sample to act as microbial growth inhibitor. The tubes were set on an end-to-end shaker for 16 hours at 150 turns per minute. At the end of the shaking process, the samples were centrifuged at 5000 rpm for 10 minutes the resultant supernatant filter through a Whatman No.5 filter paper to obtain a clear extract. The clear extracts were analysed for available P following Murphy and Riley [290]. Each adsorption process was done in quadruplets. The quantity of P adsorbed at equilibrium by treated soil samples were calculated using equation (40).

$$Q_e = \frac{(C_i - C_e)\ x\ V}{m} \tag{40}$$

Where Q_e (mg/kg) is the quantity of P adsorbed by treated soil samples, C_i (mg/L) the initial concentration of P, C_e (mg/L) the quantity of P at equilibrium after adsorption, V (L) the volume of P solution used for adsorption and m (kg) the mass of amended soil sample.

2.5.2 Data fitting of phosphorus adsorption isotherms

The experimental data of the quantity of P adsorbed at equilibrium were fitted into two important isotherm models namely Langmuir and Freundlich. Each isotherm is characterized by definite constants whose values express the surface properties and affinity of the amended soil samples. The nonlinear form of Langmuir isotherm model used is represented by equation (41) which describes single-layer adsorption:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{41}$$

Where, Q_e (mg/kg) is the quantity of P adsorbed by the soil or soil/biochar mixture, C_e (mg/L) the quantity of P at equilibrium after adsorption, Q_{max} the P adsorption maximum for Langmuir model (mg/kg), K_L the equilibrium constant that determines the binding energy (LKg^{-1}), the higher the K_L the stronger the binding force.

The nonlinear form of Freundlich is given in equation (42) below which describes multi-layer adsorption

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{42}$$

Where Q_e (mg/kg) is the quantity of P adsorbed by the soil or soil/biochar mixture, C_e (mg/L) the quantity of P at equilibrium after adsorption, K_F (mg/kg) the Freundlich constant indicating adsorption capacity not specifically the maximum adsorption capacity, and $\frac{1}{n}$ the adsorption intensity which indicates the heterogeneity of the material [277]

2.5.3 Phosphorus desorption experiment

In order to evaluate the reversibility of phosphate sorbed on soil and soil-biochar mixture, their desorption characteristic were also determine. In the first phase, 10 mL of 80 mgL^{-1} of P was shaken with 0.2 g of soil or soil/biochar mixture for 16 h on an end-to-end shaker. At the end of the sorption experiment, the supernatant was removed; the amended soil samples were obtained as the residue and dried at room temperature. Then in the second phase, the desorption experiment of P from the amended soil samples from the dried residue was done in the following manner, 0.1 g of the soil and soil/biochar was mixed with 10mL of 0.01 M KCl and agitated for 16h, then centrifuged and the supernatant was analysed for the determination of P [290]. The desorption percentage was calculated using equation (43) below:

$$Desorption\,percentage\ (\%) = \frac{P_{desorbed}}{P_{sorbed}} x100 \qquad (43)$$

Where, P_{sorbed}(mg/kg), is the quantity of P adsorbed at equilibrium and $P_{desorbed}$ (mg/kg) is the quantity of P desorbed.

2.6 Experimental protocols for analysis of some species in soils extracts

2.6.1 Spectroscopy analysis of phosphorus

Many methods have been developed for the analysis of P in soil extracts. These methods depend on the sensitivity and it is not the same when extracts have high or traces amount of P. Some methods include; atomic absorption, amperometry, potentiometry, conductimetry, coulometry and polarography, use of indirect determination, for example via molybdenum after formation of phosphomolybdate complex.

The analysis of P in its ortho form is based on the reaction of the molybdic acid with the ortho phosphate in an acid medium. A reducing compound catalysed by the antimonyl tartrate leads to the formation of the highly coloured blue complex of the phosphomolybdic anion

$$\mathrm{HPO}_{4(\mathrm{aq})}^{2-} + 12\mathrm{MoO}_{4(\mathrm{aq})}^{2-} + 23H_{(aq)}^{+} \rightarrow \underbrace{[\mathrm{PO}_4(\mathrm{MoO}_3)_{12}]^{3-}}_{\text{Blue reduced form}} + 12\mathrm{H}_2O_{(l)} \qquad (44)$$

In this work, we used a modified single solution method for the determination of phosphate in natural waters proposed by Murphy and Riley [290] which produces and intense blue complex stable for 24 h.

Preparation of reagents

- **Sulphuric acid (5 N)**

Using a measuring cylinder, 68 mL of concentrated sulphuric acid (98 %) is added to deionised water in a 500 mL volumetric flask. Then deionised water was added to the mark and then stored in a glass bottle.

- **Ammonium molydate (40 gL^{-1})**

20 g of Ammonium molydate is weighed on an electronic balance and dissolved in a 500 mL volumetric flask. The solution is well homogenised and stored in a pyrex glass bottle.

- **Ascorbic acid (0.1 M)**

On a daily basis, the solution of ascorbic acid was prepared by weighing 0.881 g of ascorbic acid and dissolving it in 50 mL deionised water in a 50 mL volumetric flask. The solution was store for that day in a dark glass bottle.

- **Potassium antimonyl tartrate (1 mg Sb/mL)**

0.2743 g of potassium antimonyl tartrate is accurately weighed and dissolved 100 mL of deionised water in a 100 mL volumetric flask. The solution was stored in a dark glass bottle.

- **The mixed reagent (Sulphomolybdic reagent)**

On a daily basis prior to analysis of P in soil extract, the sulphomolybdic reagent was prepared as follow. For the preparation of 100 mL of mixed reagent, 50 mL of 5 N sulphuric acid is thoroughly moxed with 15 mL of ammonium molybdate solution. Then 30 mL of ascorbic acid is added followed by 5 mL of potassium antimonyl tartrate solution. The solution is kept in a dark glass bottle.

- **Standard phosphate solution**

A stock solution of 50 ppm was prepared by dissolving 0.02195 g of KH_2PO_4 in 100 mL of deionised water. From this stock solution, 2 ppm solution was prepared by mixing 4 mL of the mother solution with deionised water in a 100 mL volumetric flask.

Construction of calibration range

The calibration range was constructed whenever a sample is to be analysed. In this thesis, a sample calibration range was constructed.

From this 2 ppm standard solution, different concentrations of P in 10 mL glass bottle viz. 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 ppm by pipetting volumes as presented in Table 4. To these solutions, 2 mL of sulphomolybdic solution is added. The absorbance was obtained by introducing the solution in cells and read on a UV-Vis spectrometer in the wavelength range from 500 to 1000 nm. The absorption values taken to plot the calibration curve was taken at wavelength 889 nm.

Table 4: Values for the preparation of standard solutions of P for the calibration curve

V_p	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
V_e	8	7.5	7	6.5	6	5.5	5	4.5	4	3.5	3
V_M	2	2	2	2	2	2	2	2	2	2	2
C_p	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1

V_p: volume of phosphate from 2 ppm solution, V_e: volume of water added, V_M: volume of mixed reagent added, C_p: concentration of different standard solution

From the data obtained from the UV-Visible analysis, the calibration curve and the spectrum (Figure 11) for the analysis of P was drawn the equation of straight obtain as A = 0.69464[P] – 0.00186.

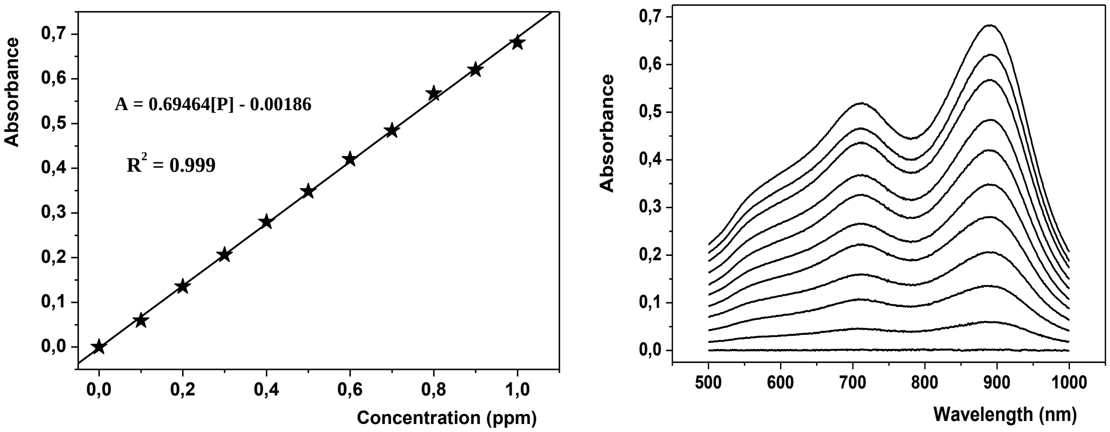
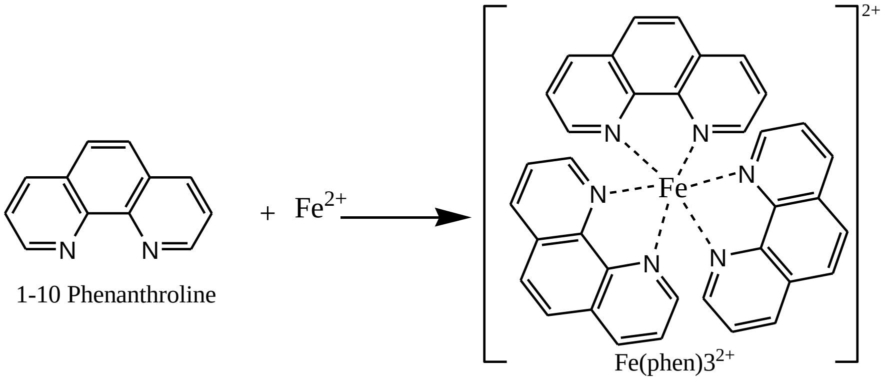


Figure 12: Calibration curve (left) and the visible spectrum (right) for the analysis of the blue complex of phosphate

2.6.2 Spectroscopy analysis of Iron(II) ions

Bhavan in 2011 [297], in his review listed several analytical methods for the analysis of iron ions. These methods include (1) spectrophotometric method, (2) chromatography method, (3) stripping voltammetry, (4) titration, (5) flow injection analysis, (6) redox determination, (7) electrochemical analysis, (8) Fluorometric analysis, (9) Chemiluminescence and (10) Polarography.

In this work, after the extraction of exchangeable Iron in aqueous solution, the spectrophotometric method was used in the determination of exchangeable Fe in the soil extract. Precisely, the phenanthroline method was used for the development of the red coloured complex which was measured at 510 nm on a UV-visible spectrophotometer.



(45)

Preparation of reagents

- **Solution of Fe^{2+} (5 mg/L)**

A mother solution of 100 mg/L of Fe^{2+} was prepared by dissolving 0.0351 g of a Mohr salt ($(NH_4)_2Fe(SO_4)_2(H_2O)_6$) in a volumetric flask. Then the daughter solution (5 mg/L) which was used for calibration line determination was prepared by diluting 5 mL of the mother solution in 100 mL of deionised water I a volumetric flask. This solution was freshly prepared to avoid it oxidation to iron(III) ions.

- **Hydroxylamine solution (1.5 %)**

0.75 g of hydroxylamine was weighed on an electronic balance and dissolved in a 50 mL volumetric flask. The solution was well homogenised and stored in glass bottles.

- **1-10 phenanthroline solution (0.2 %)**

The solution was prepared by dissolving 0.1 g of 1-10 phenanthroline crystals in 30 mL of deionized water while gentle warming the mixture. Then, cool the solution and dilute to 50 mL. The solution was stored in reagent bottles in the dark

- **0.1 M Acetate buffer Solution of pH = 4,6**

The buffer solution was prepared by mixing 0.3 g of sodium acetate with 0.3 mL of ethanoic acid in a 50 mL volumetric flask. The solution pH was adjusted using 0.1 M HCl or NaOH.

Construction of calibration range

The calibration range was constructed by ranging the concentration of the iron (II) solution. This was done by varying the initial volume of iron (II) solution. In each sample standard solution, 2 mL of hydroxylamine was added to reduce any existing Fe^{3+} ion to Fe^{2+} ions. Then 5 mL of acetate buffer solution was added followed by a certain volume of water, and finally 3 mL of 1-10 orthophenanthroline. After 10 min, the mixture was analysed on a UV-visible spectrophotometer, and the absorption recorded at a maximum wavelength of 510 nm.

Table 5: values for the preparation of standard solutions of Fe^{2+} for the calibration curve

V_p	0	0.2	0.4	0.8	1.2	1.6	2	2.4	2.8
V_1	2	2	2	2	2	2	2	2	2
V_2	5	5	5	5	5	5	5	5	5
V_3	10	9.8	9.6	9.2	8.8	8.4	8.0	7.6	7.2
V_4	3	3	3	3	3	3	3	3	3
C_p	0	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7

V_p: volume of Fe^{2+} from 5mg/L solution, V_1: volume of hydroxylamine added, V_2: volume of acetate buffer added, V_3: volume of deionised water added, V_4: volume of 1-10 phenanthroline solution added, C_p: concentration of different standard solution

From the data obtained via the UV-Visible analysis, the calibration (Figure 12) curve and the spectrum for the analysis of P was drawn the equation of straight obtain as A = 0.1949[Fe^{2+}] – 0.0019.

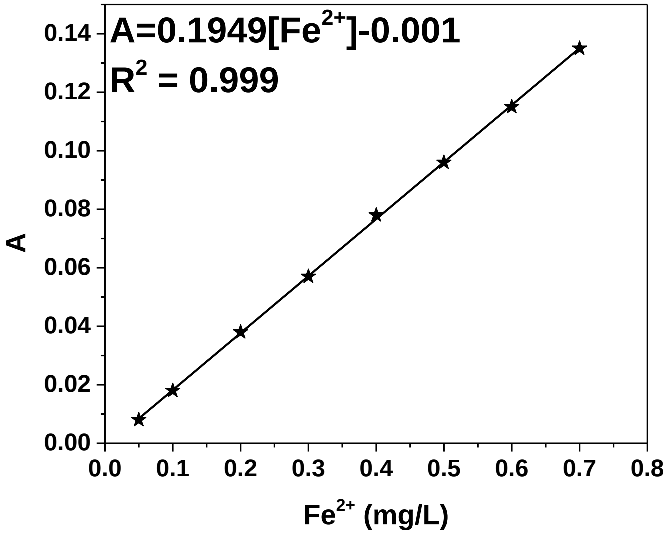


Figure 13: Calibration curve for the analysis of Fe using phenanthroline

2.7 Statistical analysis tool

Statistical analyses were perfomed using Excel 2013 and graphics using Origin 8.5. A One-way analysis of variance was performed for each incubation time interval, amendment rate, biochar type, and a Two-way analysis of variance was performed by crossing the following dependent factors: incubation time interval, amendment rate, and biochar type. The significant difference between the factors means for parameters under analysis were determined at a 5% level of significance ($\alpha = 0.05$). A Pearson correlation and t-test was performed to measure the strength of correlation and significance of the factors on the parameters under study.

Non-linear regression analysis was used to fit Langmuir and Freundlich isothermal equations to data. Curve fitting and statistical analyses were done using Origin 8.5. The goodness of fit was evaluated based on coefficient of determination (R^2).

2.7.1 Mean

The mean ($\bar{x}$) is simply the sum of all the values divided by the number of values. It is the most commonly used measure of central tendency [298]. It is calculated using the formula in equation (16)

$$\bar{x} = \frac{\sum x}{n} \quad (16)$$

Where $\sum x$ is used to denote the sum of all observations, and n is the total frequency or number of values

2.7.2 Analysis of Variance

Analysis of variance (ANOVA) is a conceptually simple, powerful, and popular way to perform statistical testing on experiments that involve two or more groups [299]. It is based mathematically on linear regression and general linear models that quantify the relationship between the dependent variable and the independent variables(s) [300].

The common terminologies used in ANOVA include:

- **Dependent variable**

This is the item being measured that is theorized to be affected by the independent variables.

- ***Independent variable(s)***

These are the items being measured that may have an effect on the dependent variable. In ANOVA terminology, an independent variable is called a factor.

- ***Grand mean***

The grand mean is the mean of sample means or the mean of all the observation, irrespective of the sample

$$\bar{x} = \frac{\sum_i \bar{x}_i}{n} \tag{17}$$

Where $\bar{x}_i$ is the mean of sample i and n the total number of means of sample means

- ***Hypothesis***

A hypothesis is an educated guess about something. It can be testable either by experiment or observations. There are two types of hypothesis; (i) the Null hypothesis (H_0) which is the commonly accepted fact. In ANOVA, the null hypothesis is valid when all the sample means are equal, or they don't have a significant difference ($\bar{x}_1 = \bar{x}_2 = \bar{x}_3 \dots = \bar{x}$). (ii) The Alternate hypothesis (H_1) states your research prediction of an effect. The alternate hypothesis is valid when at least one of the sample mean is different from the rest of the sample means ($\bar{x}_1 \neq \bar{x}$) [301].

- ***p- value***

The *p*-value or the probability value is a number, calculated from a statistical test, that describes how likely to found a particular set of observations if the null hypothesis were true. *P*-values are used in hypothesis testing to help decide whether to reject the null hypothesis. The smaller the *p*-value, the more likely the null hypothesis is rejected. The *p*-value is a proportion: if your *p*-value is 0.05, that means that 5% of the time you would see a test statistic at least as extreme as the one you found if the null hypothesis was true [302].

- ***Statistical significance***

The statistical significance is another way of saying that the *p*-value of a statistical test is small enough to reject the null hypothesis of the test. The most common threshold is $p < 0.05$; that is, when you would expect to find a test statistic as extreme as the one calculated by your test only 5% of the time. The threshold value for determining statistical significance is also known as the alpha value. When the p-value falls below the chosen alpha value, then we say the result of the test is statistically significant.

- ***One-way analysis of variance***

The one-way analysis of variance is also known as single-factor ANOVA. It is suitable for experiments with only one independent variable (factor) with two or more levels. For example, you could use a one-way ANOVA to understand whether there is an interaction between amendment rate and soil pH, where amendment rate is the independent variables, and soil pH is the dependent variable. The one-way ANOVA is used to determine whether there are any statistically significant differences between the means of three or more independent (unrelated) groups. It compares the means between the groups you are interested in and determines whether any of those means are statistically significantly different from each other.

- ***Two-way analysis of variance***

The two-way ANOVA compares the mean differences between groups that have been split on two independent variables (called factors). The primary purpose of a two-way ANOVA is to understand if there is an interaction between the two independent variables on the dependent variable. For example, you could use a two-way ANOVA to understand whether there is an interaction between amendment rate and number of incubation days on soil pH, where amendment rate and number of incubation days are the independent variables, and soil pH is the dependent variable.

2.7.3 Pearson correlation

The Pearson correlation measures the strength of the linear relationship between two variables. It has a value between -1 to +1, with a value of -1 meaning a total negative linear correlation, 0 being no correlation, and + 1 meaning a total positive correlation [303]. That is, the sign of the coefficient indicates the direction of the relationship. If both variables tend to increase or decrease together, the coefficient is positive, and the line that represents the correlation slopes upward. If one variable tends to increase as the other decreases, the coefficient is negative, and the line that represents the correlation slopes downward [304]. It is mostly calculated using softwares like Excel, SPSS, Origin 8 and others, but the mathematical equation is given by

$$r_{xy} = \frac{cov(x,y)}{\sqrt{var(x)}.\sqrt{var(y)}} \tag{18}$$

Where $cov(x, y)$ is the sample covariance of x and y, $var(x)$ is the sample variance of x, and $var(y)$ is the sample variance of y.

To determine whether the correlation between variables is significant, the p-value is compared to the significance level. Usually, a significance level (denoted as α or alpha) of 0.05 works well. An α of 0.05 indicates that the risk of concluding that a correlation exists when, actually, no correlation exists is 5%. The p-value informs whether the correlation coefficient is significantly different from 0. (A coefficient of 0 indicates that there is no linear relationship.). When the p-value less than or equal to the significance level, then it is concluded that the correlation is different from 0, thus the correlation is statistically significant and when the p-value is greater than α, it cannot be concluded that the correlation is different from zero, thus, the correlation is not statistically significant [305].

CHAPTER 3

RESULTS AND DISCUSSION

This Chapter has three main aims which include: (i) Characterization of soil and biochar samples; (ii) Analysing the effect of biochar amendment on the chemical properties of the sampled acid soil; and (iii) phosphorus fixation and release in acid soils amended with biochar.

3.1 Characterization of soil and biochar samples

3.1.1 Characterization of soil samples

Characterisation of soil samples is important prior to any amendment studies. This enables the researcher to predict the effect of the amendments and its consequences on the soil.

Physical properties of soil such as the bulk density reflect the size, shape and arrangement of particles and voids. It is a good indication of the suitability for root growth and soil permeability and is vitally important for the soil-plant-atmosphere system [306]. From Table 6, the bulk density was 0.9 g/cm^3. This bulk density is good, because it is reported that soil with bulk density less than 1.5 g/cm^3 is desirable for optimum movement of air and water through the soil [307]. The soil porosity was above 50 %, (55.04% as in Table 6) and gave information on how much air and water can be stored in the soil profile. The soil bulk density and soil porosity is related to the soil texture and amount of organic matter. The sample soil texture was loamy (Table 6), which corroborates with the low bulk density which has good structure, high pore space [308] rather than with the amount of organic matter which is low for this soil sample. To further decrease the soil bulk density which will be favourable to soil function, residue and tillage management should be applied. The residue management could be the addition of materials with large and many pores such as biochar.

Table 6: Characteristics of sample soil

BD (g/cm^3)	SWC (g/g)	SP (%)	PSD (%)			ST	pH	EC (µS/cm)	Ex Acidity (cmol$^+$/kg)	Avai. P (mg/kg)	OC (mg/kg)
			Silt	Sand	Clay						
0.90	0.39	55.04	42.9	33.3	23.8	Loamy	4.70	53.20	3.05	16.10	1.12

BD = Bulk density; SWC = Soil water content; PSD = particle size distribution; ST = soil texture; EC =Electrical conductivity; Ex = Exchangeable; Avai. Available; OC = Organic carbon

The soil sample was acidic, with soil pH of 4.70 less than 6.5 and with exchangeable acidity of 3.05 cmol/kg (Table 6). Soils in Western and Southern Cameroon are acidic due to the presence of high level of exchangeable Al and Fe [176,187]. This low soil pH can also be due to the application of nitrogenous fertilizers due to the fact that the sample soil was found in a mixed coffee and cocoa farm which have been receiving nitrogenous fertilizers over years. The high level of acidity impacted the amount of available P (16.10 mg/kg) by immobilizing it through fixation in soil.

3.1.2 Characterization of biochar samples

- **Biochar Yield and Ash content**

Table 7 illustrate the results of biochar yield and ash content which varies with biochar type and pyrolysis temperature. The biochar yield of coffee husk and cocoa pod husk reduced significantly ($p < 0.05$) from 38.7% to 30.3 % and 38.4% to 32.0% for pyrolysis temperature of 350 and 550 °C respectively. The decrease in yield is due to the volatilization of C, O and H compounds [309]. This can be observed on the FTIR spectra of biochar produced at 550 °C with the disappearance of bands corresponding to the $–CH_2$ and OH functional groups (Figure 15). The disappearance is due to the dehydration and thermal degradation of cellulose and hemicellulose to gases such as CH_4, H_2, and CO [68,309,310]. This trend in yield, decreases due to increase in temperature for coffee husk and cocoa pod husk are consistent with works of Domingues and collaborators [311], and also Tsai and collaborators [312]. Thus, biochar yield depends on the source of feedstock and the pyrolysis temperature. The percent yield obtain is quite interesting and can be economically good for production by small scale farmers.

Table 7: The yield and ash content of produced biochars

Biochar samples	CH350	CH550	CP350	CP550
Yield (%)	38.7 ± 0.70	30.3 ± 0.70	38.4 ± 0.60	32.0 ± 2.00
Ash (%)	16.68 ± 0.21	24.05 ± 0.42	21.93 ± 0.12	29.01 ± 0.26

Ash content varied with biochar type and pyrolysis temperature. From Table 7 it is observed that biochar from coffee husk has less ash content compared to biochar from cocoa pod husk for the same pyrolysis temperature. For cocoa pod husk biochar, ash content increases significantly ($p < 0.05$) with temperature from 16.68% to 24.05% same as for cocoa pod husk biochar whose ash content increased significantly ($p < 0.05$) from 21.93% to 29.01%. The increase in ash content is due to the condensation of mineral elements/compounds [309,313] which is confirm with the increase in peaks of minerals observed on the XRD spectrum. Also, due to the degradation of the organic part of the biomass as can be seen on the FTIR spectra. Cocoa pod husk biochar has a greater ash content compare to coffee husk biochar due to the presence of more minerals (quartz, kalicinite, sylvite, and calcite) as can be confirmed from the XRD analysis. These results are consistent with other reported in the literature such as an increase in ash content from 12.9% to 19.6% for an increase in temperature from 450 to 750 °C [311].

- **Biochar pH, EC and $CaCO_3$ equivalent**

All biochars were alkaline with pH greater than 7 and the pH were virtually the same for all pyrolysis temperature (Table 8). High pH values of cocoa pod husks and coffee husk biochar have been reported in previous work. Martinsen and collaborators [292] recorded a pH value of 10.5 for biochar obtain from cocoa pod husk while for coffee husk, a pH of about 10 was recorded by Domingues and co-workers[311]. The alkaline nature with high pH values can be due to the presence of greater quantities of ash (Table 7), alkali salts, carbonates, and bicarbonates (XRD spectra, Figure 16). Moreover, at higher pyrolysis temperature, there was a reduction in the concentration of acidic functional groups [291] and the formation of basic surface oxides [79].

Table 8: Biochar pH, EC and $CaCO_{3(eq)}$

Biochar samples	CH350	CH550	CP350	CP550
pH	9.33 ± 0.01	9.69 ± 0.01	9.53 ± 0.02	9.63 ± 0.01
EC (mS/cm)	9.66 ± 0.60	20.65 ± 0.21	18.06 ± 0.20	30.50 ± 0.28
$CaCO_3$ *eq* (%)	4.02 ± 0.01	12.09 ± 0.11	10.13 ± 0.01	14.17 ± 0.13

Analysis of biochar electrical conductivity is to estimate the amount of soluble salts in the biochar in order to avoid producing an adverse effect on salt sensitive plant due to high soil salinity [20]. Electrical conductivity significantly ($P < 0.05$) varied with biochar type and significantly ($p < 0.05$) increases with pyrolysis temperature (Table 8). Cocoa pod husk biochar have greater electrical conductivity values as compared to coffee husk biochar for the same pyrolysis temperature. Electrical conductivity increases from 9.66 to 20.65 mS/cm and from 18.06 to 30.50 mS/cm for an increase in pyrolysis temperature from 350 °C to 550 °C for coffee husk and cocoa pod husk respectively (Table 8). Biochar produced at a high temperature generally has higher electrical conductivity values [28,314]. This situation has been attributed to the increasing amount of ash which contains high amounts of soluble salts (in this case sylvite and biocarbonates of potassium present in the biochar) caused by the loss of volatile material during pyrolysis [314]. Moreover, biochar produced from different feedstock may result in different electrical conductivity values due to their ash contents [28]. Cocoa pod husk biochar contain higher amount of ash than coffee husk (Table 7) due to the high amounts of potassium which can be obtained from great quantity of sylvite and kalicinite (XRD spectrum) [313].

The concentration of carbonates can be valued in biochar as liming equivalence. It was observed that liming equivalence increases significantly ($p < 0.05$) with pyrolysis temperature for both biochars. Moreover, cocoa pod husk biochar had a greater liming equivalence than coffee husk biochar for the same pyrolysis temperature (Table 8). Higher liming value in cocoa pod husk biochar as compared to coffee husk biochar at pyrolysis temperature of 350 °C is due to a high level of carbonates and bicarbonates of calcium and potassium respectively as can be observed on the XRD spectra. An increase in pyrolysis temperature was correlated with an increase in liming equivalence due to the accumulation of minerals, increase in ash content (Table 7), and bicarbonates and carbonates (XRD spectra; Figure 16). High liming value has been previously reported, indicating the presence of calcite and other carbonate minerals in these biochars can be a source of lime [292,311]

- ***Acid-base titration curve to evaluate biochar alkalinity and acid neutralising capacity.***

The acid-neutralising capacity of cocoa pod husk biochar was higher than those of coffee husk biochar irrespective of pyrolysis temperature (Table 9). A significant ($p < 0.05$) increase in acid-neutralizing capacity was observed for both biochars with increasing temperature. Compare to lower temperature it was almost the double; this may be due to an increase in alkaline component such calcite, kalicinite (XRD spectrum; Figure 16) whose role is to consume H^+ ions in solution. Also, the acid-neutralizing capacity at lower temperature can be caused by the presence of $–O^-$ and/or $–COO^-$ groups present which can fix H^+ in solution. So we can hypothesize a greater H^+ consumption by cocoa pod husk biochar in acid soils as compare to coffee husk biochar for the same temperature of pyrolysis.

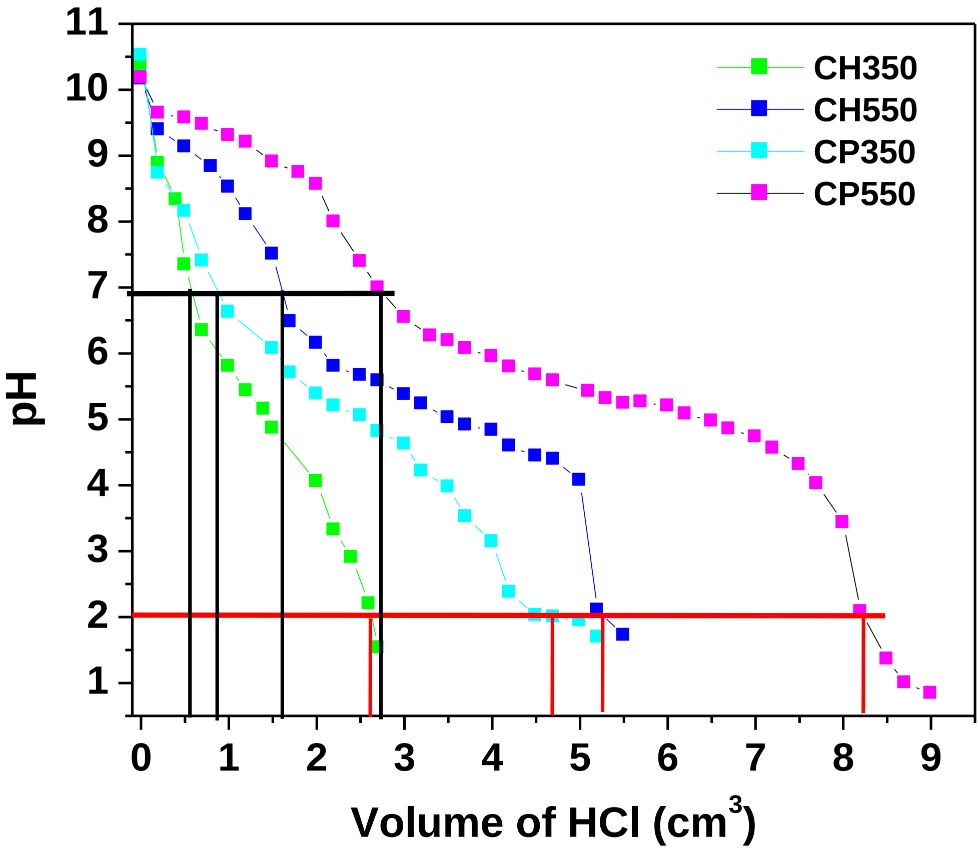


Figure 14: Acid-base titration curves of biochars produced from coffee husk and cocoa pods at different pyrolysis temperature.

From Table 9, the data obtained indicates that all four biochars are alkaline, with alkalinity varying with pyrolysis temperature and biomass type. Data in Table 9 gives the biochar alkalinity when titrated to pH 7.0 and 2.0 and calculated from Figure 13. Biochar produced from cocoa pod husk has alkalinity almost twice that of biochar produced from coffee husk. In order to probe the origin of the biochar alkalinity, a potentiometric titration was done to obtain the acid-base titration curves. The titration curves for biochars produced at low temperatures were straight lines while those produced at 550 °C shown a plateau between some pH ranges. The plateau occurred for CH550 and CP550 with a larger plateau and starts at a higher pH value for the latter than the former. For CH 550, the plateau was from pH 6.3 to 4.2 which covers 2.1 unit for volume of HCl consumption (Figure 13), whereas for CP550, the plateau ranges from pH 6.5 to 4.0 covering 2.5 units. The plateau region observed for biochar produced at 550°C, suggests a relatively higher buffer capacity for acids in the pH range at which the titration curve plateau occurred [86].

Table 9: Biochar alkalinity at pH 7 and 2 and acid-neutralisng capacity for all four biochars

Biochar samples		CH350	CH550	CP350	CP550
Biochar alkalinity (cmol$^+$kg^{-1})	pH =7	15.2	42.7	22.7	71.7
	pH =2	70.4	140.5	120.3	219.7
Acid-neutralizing capacity (Cmol(H$^+$)/kg)		151.9 ± 2.3	252.5 ± 2.3	198.1 ± 3.7	340.7 ± 5.4

- ***Available phosphorus and organic carbon content***

Biochar produced in this study can be considered as a source of Available P. Table 10 consigns the quantity of available P and organic carbon presents in the four biochars. Available P is higher in biochar produced from cocoa pod husk than those produced from coffee husk. Results from past research have proven biochar as a source of P [118,119]. From Table 10, it is observed that, the quantity of organic carbon decreases with temperature of biochar production. This can be explained by the fact that as pyrolysis temperature increases, the resultant biochar tend to contain more recalcitrant carbon (graphitised).

Table 10: Quantity of available P and organic carbon in the four biochars

Biochar samples	CH350	CH550	CP350	CP550
Available P (mg/kg)	866.02 ± 2.4	954.54 ± 23.18	1232.45 ± 16.34	1076.90 ± 42.25
Organic carbon content (g/kg)	67.10 ±1.10	6.67 ± 0.30	76.10 ± 1.40	11.01 ± 0.10

- ***Infra-red spectra***

In the FTIR spectra presented (Figure 15 (A) for CH350 and CH550 and Figure 15 (B) for CP350 and CP550) various functional groups are observed. All four biochar presented a broad band centered at 3418 cm^{-1}, which was attributed to the O–H stretching vibration of hydrogen-bonded hydroxyl groups from phenolic, carboxylic or alcohol hydroxyl group [315]. The band shape was more pronounced in CH350 and CP350 than in CH550 and CP550 probably due to the breakdown of hydroxyl groups [316]. The band at 2925 cm^{-1} and 2966 cm^{-1} on the spectra of CH350 and CP350 respectively corresponded to the asymmetric C–H stretching vibration in aliphatic compounds suggesting the presence of cellulose and hemicellulose [310,315], the band almost disappears on the CH550 and CP550 spectra due to its decomposition on increase in temperature [317]. The absorption bands appearing at wavenumber 1594 cm^{-1}; 1577 cm^{-1} very intense on CH350 and CP350 and 1559 cm^{-1};1576 cm^{-1} less pronounced on CH550 and CP550 corresponded to the C=C aromatic stretching and C=O stretching of conjugating ketones and quinones [318]. It should be noted that the band intensities are surprising since it is always observed that the band intensity increases with rise in temperature due to increase in aromaticity, but in this case, it is the reverse which could be explained by an increase in ash content of the biochar at a higher temperature which causes the aromatic compounds to be diluted in it [316]. The absorption bands at 1410, 874, and 702 cm^{-1} for CH550 1406 cm^{-1}, 872 cm^{-1}, and 694.1 cm^{-1} for CP550 corresponded to the in-, out plane bending and asymmetric stretching vibrations respectively of C–O–C which indicate the presence of calcite and other mineral carbonates mineral in the biochar [319,320]. These bands were not observed in CH350 and CP350 due to very low carbonate content as observed with the $CaCO_{3(eq)}$ equivalence (Table 01). The band at 1376 cm^{-1} for CH350, 1378 cm^{-1} for CP350 indicated the presence of O-H bending mode, 618 cm^{-1} both for CH350 and CP350 for the deformation out-of-plane of the C-O-H bond of phenol [309,314]. These bands disappeared due to thermal decomposition and cleavage of organic groups with increasing temperature [321]. In CH350, there is the appearance of a band at wavenumber 1318 cm^{-1} which corresponds to the C–N stretching of aromatic amines [316] which disappears in CH550 due to the decomposition of aromatic amines at high temperature. 1116 cm^{-1}, and 1035 cm^{-1} for CH350 and CH550 and 1118 cm^{-1} and 1035 cm^{-1} for CP350 and CP550 corresponded to the absorption bands attributed to symmetric C–O stretching in lignocellulose, cellulose, hemicellulose, and lignin [315]. The bands were less pronounced CH550 and CP550 owing to the destruction of the abovementioned structure due to increase in temperature. Additionally, with the presence of high level of quartz observed in the XRD pattern for CH550 and CP550, the bands at 1007 cm^{-1} and 832 cm^{-1} were attributed to silica [315] and the wavelength at 541 and 471 cm^{-1} suggested the C-X stretching vibration (Halocarbon compounds) such as organochlorine [309].

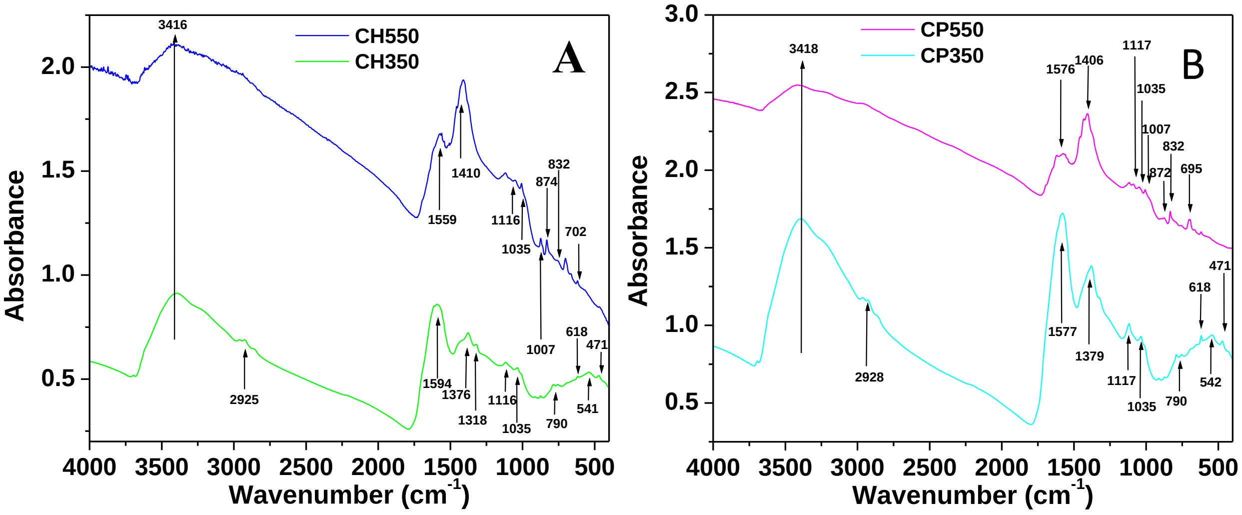


Figure 15: The Infrared spectra of coffee husk (A) and cocoa pods (B) biochar produced at different pyrolysis temperature.

Biochar production temperature affected the existing functional groups due to the dehydration of the ligneous and cellulosic contents and reduction in the aliphatic group with an increase in temperature of production. Furthermore, increase in temperature resulted in the presence of inorganic functional groups (carbonates) which is consistent with the increase in ash content and the presence of more crystalline minerals as seen on the XRD pattern.

- ***X-ray patterns***

The biochar produced presented a variety of mineral crystals, with more in biochar produced at 550 ºC than those at 350 ºC. The X-ray pattern of all four biochar showed a broad hump structure (2θ = 15-30°) which confirms the presence of a largely poorly crystalline carbon-rich phase, due to increase in the aromatic carbon [291,319]. The intensity of the dome between 15-30° decreases with rise in temperature indicating the increase in the crystallinity of the carbon-rich phase. Also, the small dome at 2θ =40-45° for biochar produced at 550 ºC indicates the presence of graphite structure [322] with a confirmed peak on CH550 (Figure 16(A) and CP550 (Figure 16 (B)) at 1.66 Å. For biochar produced from coffee husk, common peaks appeared in both spectra of CH350 and CH550 (Figure 16 (A)) at 4.25, 3.34, 1.54 Å which were attributed to quartz (Q) [70]. Unlike in CH350, where quartz is observed at pyrolysis temperature of 350 °C, Domingues and co-workers [311] did not observe quartz, but in contrary, they observe more sylvite (S) crystals. On CP350 X-ray pattern (Figure 16(B)), we observed the appearance of calcite (3.03, 2.50, 2.08Å), [323] quartz (3.35 Å) [324], kalicinite (2.97Å) and sylvite (2.22 Å).

When the pyrolysis temperature was increased (CH550), calcite (C) and kalicinite (K) were observed with sharp intense peaks at 3.03, 2.29 and 2.03Å for calcite [86] and 3.67, 2.96, 2.86 and 2.63 Å for kalicinite [70] and for CP550 most of the peaks were relatively intense indicating the presence of more crystalline mineral phases such as the sharp and intense peaks of kalicinite (3.67, 2.97, 2.85, 2.62, 2.37Å) and calcite (3.03, 2.50, 2.29Å, 2.08Å). The increase presence of kalicinite and calcite at 550 ºC may have been favoured by the reaction of K and Ca with CO_2 released during the thermal decomposition of hemicellulose and cellulose [325]. This observation was consistent with the acid-base titration curve for evaluation of biochar alkalinity (Figure 13) with a plateau for CH550 and CP550 due to buffering action of carbonates and also higher $CaCO_3$eq(%) (Table 8). Also, on CH550 x-ray pattern, several sharp and intense peaks indicating the presence of quartz (4.25, 3.34, 1.54, 1.38Å) suggesting that the quartz was well crystallised [324]. Minor peaks of quartz (3.35, 1.52Å) and sylvite (3.15, 2.22 and 1.84Å) also appeared on CP550 x-ray pattern. Other minor mineral were observed lansfordite (L, $MgCO_3.5H_2O$) at 4.16, 2.81 and 1.75Å and antigorite (A), $(Mg,Fe)_3Si_2O_5(OH)_4$) at 7.32Å. Works have showed that increase in temperature results in more mineral phases especially calcite [86].

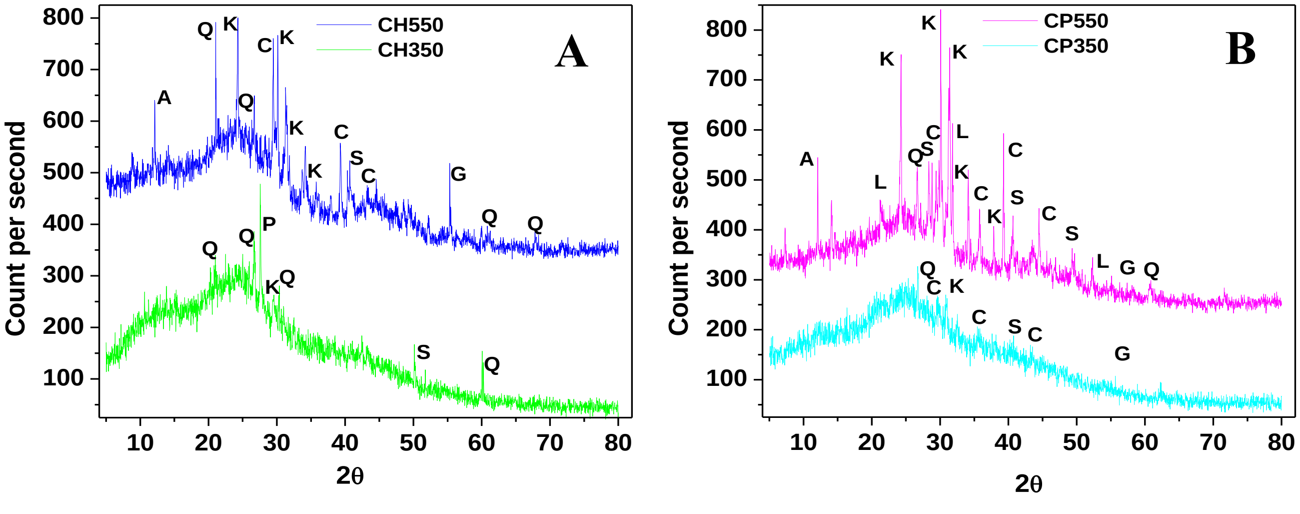


Figure 16: The x-ray pattern spectrum of coffee husk (A) and cocoa pods (B) biochar produced at different pyrolysis temperature.

- **Micrographs images -Energy dispersive spectroscopy**

Scanning electron microscopy images of biochars produced at 350 and 550 °C are shown in Figure 16 at magnifications 500X, 1000X, 1500X, 2000X and 3500X. The biochars displayed a heterogeneous surface morphology and a complex structure. The structure presented cracks, pores and crevices with irregular forms, randomly distributed and of different diameters. Biochar produced at 550 °C have rougher surface due to the presence of white particles resulting from the accumulation of minerals form at higher temperatures. Pores on cocoa pod husk biochar were more regular in size as compare to coffee husk due to the better crystallinity of cocoa pod husk biochar. The presence of pores, cracks and crevices has possible effects on soil water retention, rooting patterns, soil aeration, nutrients sorption and habitat for soil biota [31,326,327].

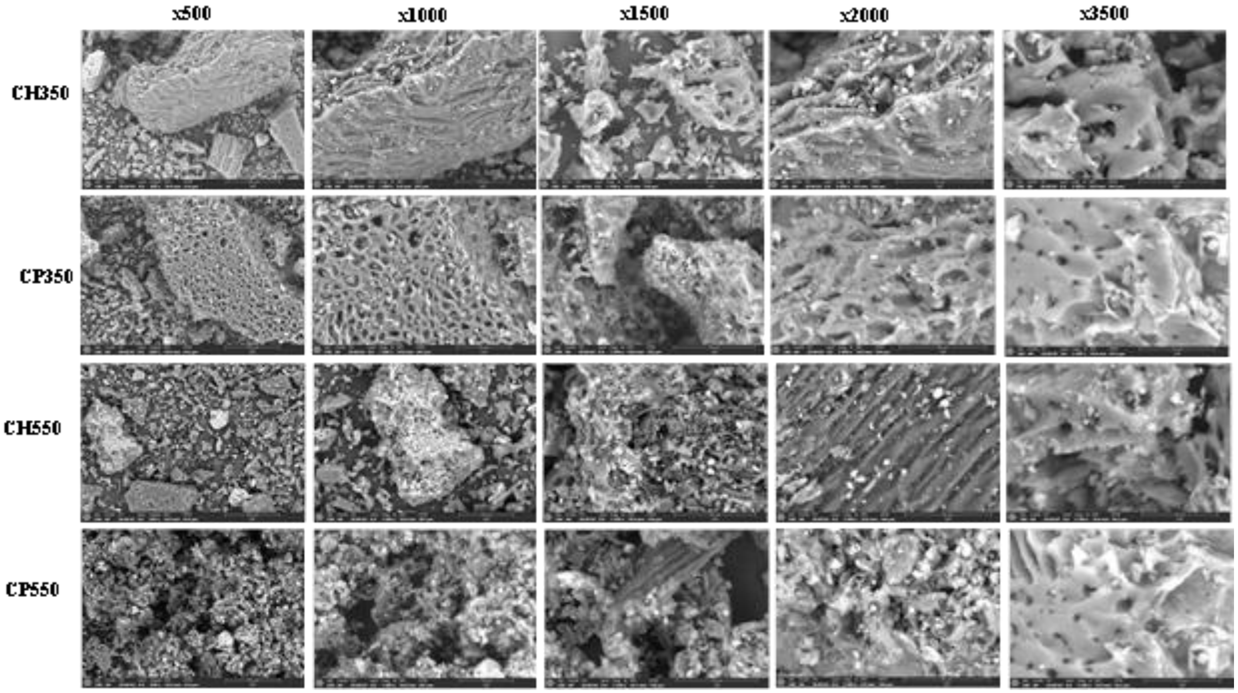


Figure 17: Micrograph images of all four biochar at different magnification power

The SEM analysis was coupled with EDS analyses for chemical mapping of elements on different biochar samples and the data extracted are consigned in Table 11. Figure 17 and Figure 18 representing the EDS spectra of biochars show distribution patterns of minerals. The spectra show intense peaks for carbon which increases with rising pyrolysis temperature. Also, a drop in the peaks level for oxygen was observed with increasing temperature. A remarkable peak of Indium was noticed in all four biochar.

In Table 11, we observe a rise in C content and drop in O with increasing pyrolysis temperature. The O/C ratio content as determined with SEM-EDS decreases with increase pyrolysis temperature production of the biochar. This result is in accordance with previous results summarized by Ahmed and collaborators [328]. Other elements present were P and Mg whose presence in biochars makes them a potential liming and fertilizing agent [24]. The presence of Indium (in high percentage) may be due to the fact that it is a trace element found in the soil, especially unpolluted soil, that can be absorbed into plants and hence food chain [329].

Table 11: Elemental compositions (%) obtain from SEM-EDS analysis and the O/C ratio.

Sample	C	O	P	Mg	Cl	Si	Al	Fe	Nb	In	S	Sb	Au	O/C
CH350	47.87	20.05	/	0.18	0.09	/	0.24	/	/	26.77	0.25	3.87	0.69	0.42
CH550	43.87	17.39	/	0.39	/	0.51	0.60	/	/	32.42	/	4.83	/	0.40
CP350	47.96	31.93	0.32	0.85	/	0.38	0.50	0.12	0.75	14.82	0.12	2.24	/	0.70
CP550	55.08	25.72	0.27	1.36	/	0.23	0.25	0.09	/	14.45	0.16	2.40	/	0.47

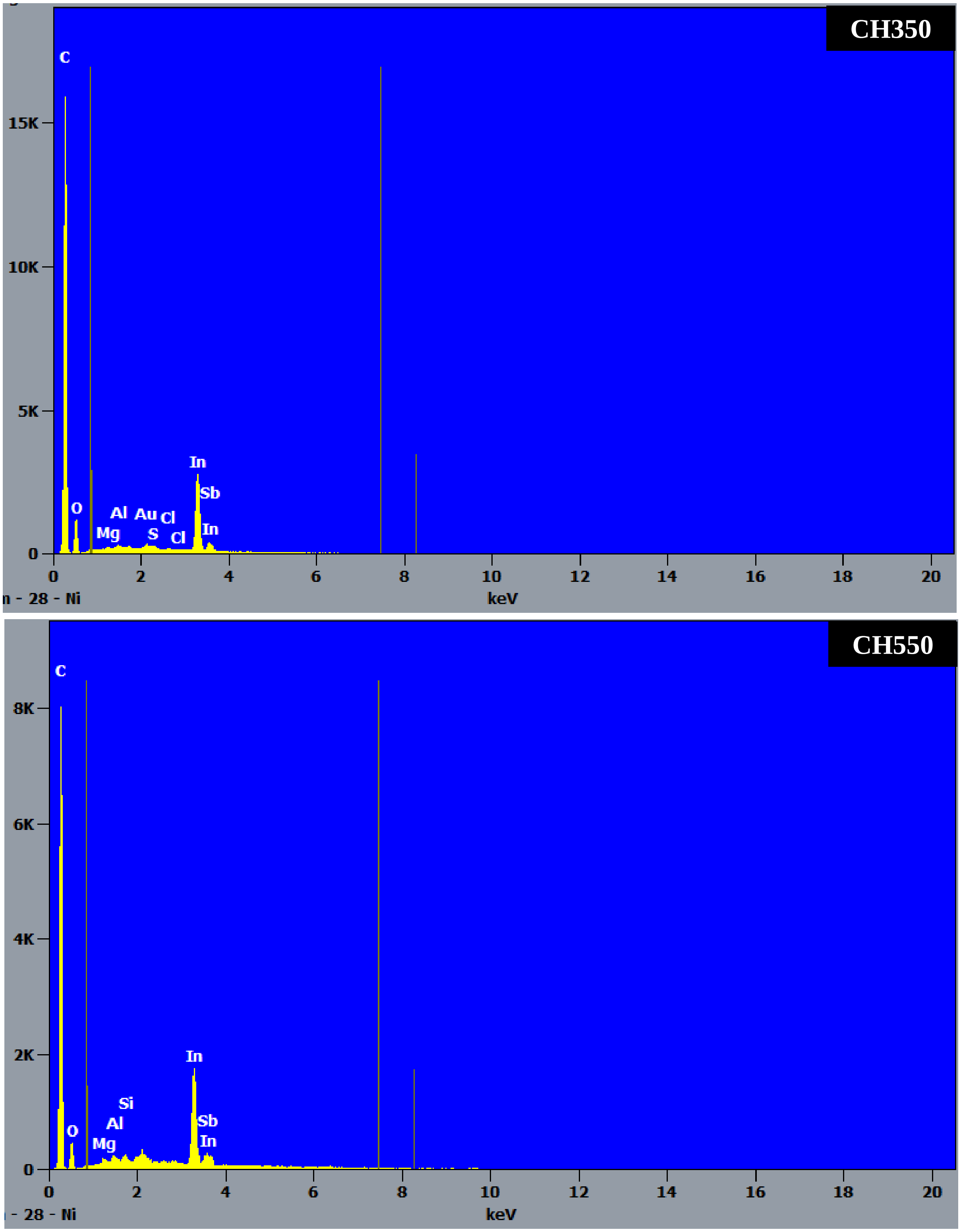


Figure 18: EDX spectra for coffee husk (CH350 and CH550)

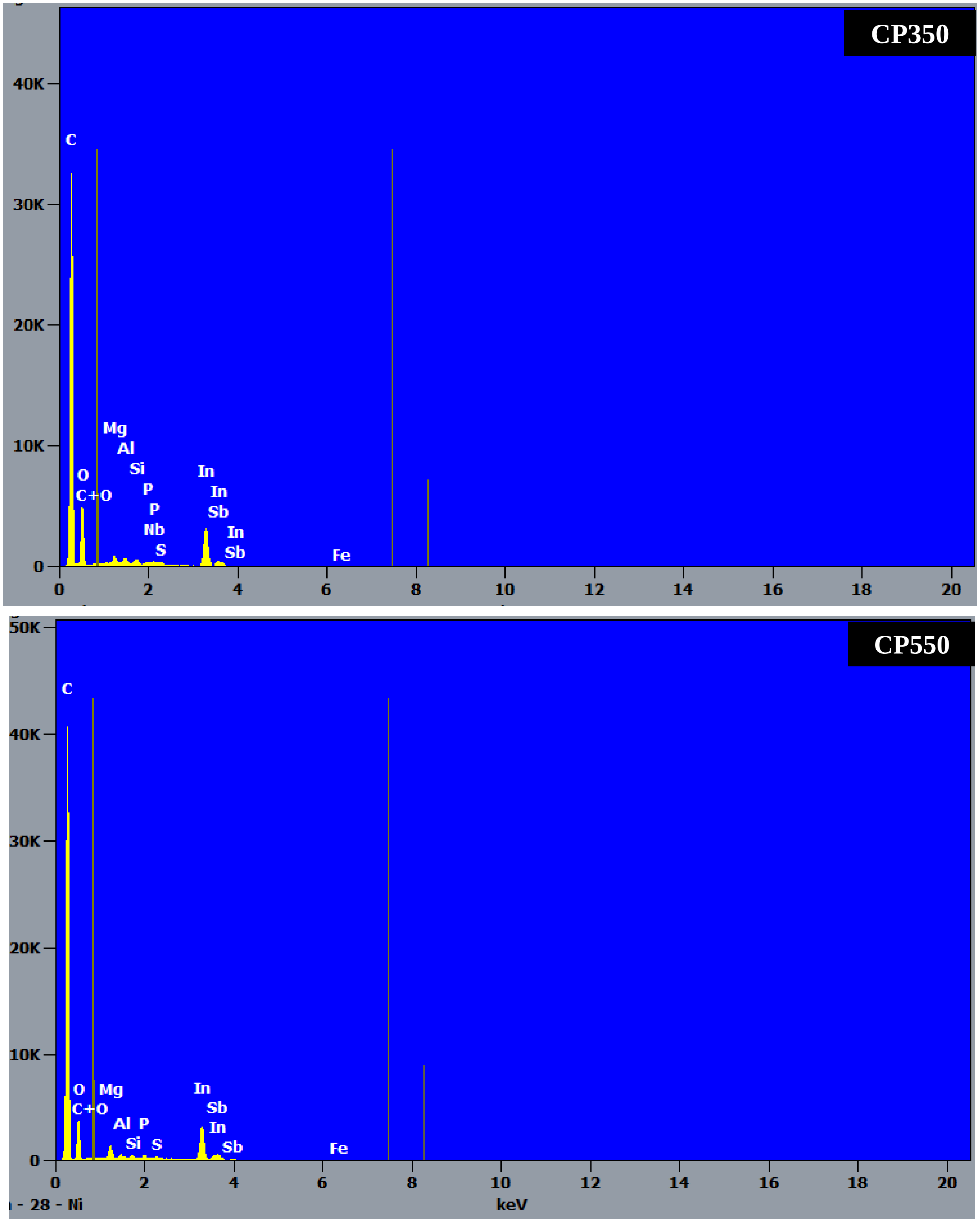


Figure 19: EDX spectra for cocoa pod husk (CP350 and CP550)

3.1.3 Partial conclusion

Biochar characterizations reveal that its properties depend on the biomass type and the pyrolysis temperature. Biochar produced from cocoa pod husk had a higher liming potential as compared to coffee husk and increasing temperature of pyrolysis resulted to the same trend in liming potential. Complexing and basic functional groups were found to exist on the surface of the biochar coupled with the presence of many minerals. The alkaline nature was admitted from the biochar pH and acid-neutralizing capacity of the biochar. The nutrient availability was as a result of the availability of P. Indeed, at the end of analysis, P was release from the biochar in aqueous solution, and thus biochar can be source of P to the soil.

3.2 Effect of biochar on the chemical properties of acid soils

3.2.1 Effect on soil pH

The effect of the number of incubation days and biochar type on soil pH upon amendment of acid soil with biochar is presented in Figure 20. The application of biochar from coffee husk and cocoa pod husk on acid soil had a significant effect ($P < 0.05$) on the increase in soil pH as compared with control. Biochar from cocoa pod husk raises the soil pH to higher values as compare to biochar produce from coffee husk and besides, biochar produce at 550 ºC yielded a higher increase in soil pH than those produced at 350 ºC. In a nutshell, after incubation of acid soils with all four biochars at the rate of 20 g/kg, 40 g/kg, and 80 g/kg, the soil pH was affected significantly ($P < 0.05$) over incubation time. Precisely, for amendment rate of 80 g/kg, CH350 and CP350, a significant effect on soil pH ($p < 0.05$) was observed unlike for CH550 and CP550 where no significant effect on the variation of incubation time on soil pH ($p > 0.05$) resulted. Also, Figure 20 presents the effect of amendment dosage application on soil pH. An increase in biochar amendment rate for all four biochars, increased the soil pH significantly ($P < 0.05$). In addition, the greatest effect of biochar on soil pH was from cocoa pod produced at 550 °C at a rate of 80 g/kg which cause the soil pH to increase up to about pH 8. The increase in soil pH due to incubation of biochar was precisely due to the increase in the alkaline characteristic of the biochar. Furthermore, the combined effect of amendment rate and incubation time had a significant effect on the increase in soil pH ($P < 0.05$) for each number of incubation days. The greater sensitivity of CP550 which increases soil pH at the start of incubation and maintains the high level was observed by Martinsen and collaborators [292]. Making cocoa pod husk biochar higher potential liming agents compare to coffee husk biochar due to greater alkalinity, higher $CaCO_3$eq(%) and a greater acid-neutralizing capacity.

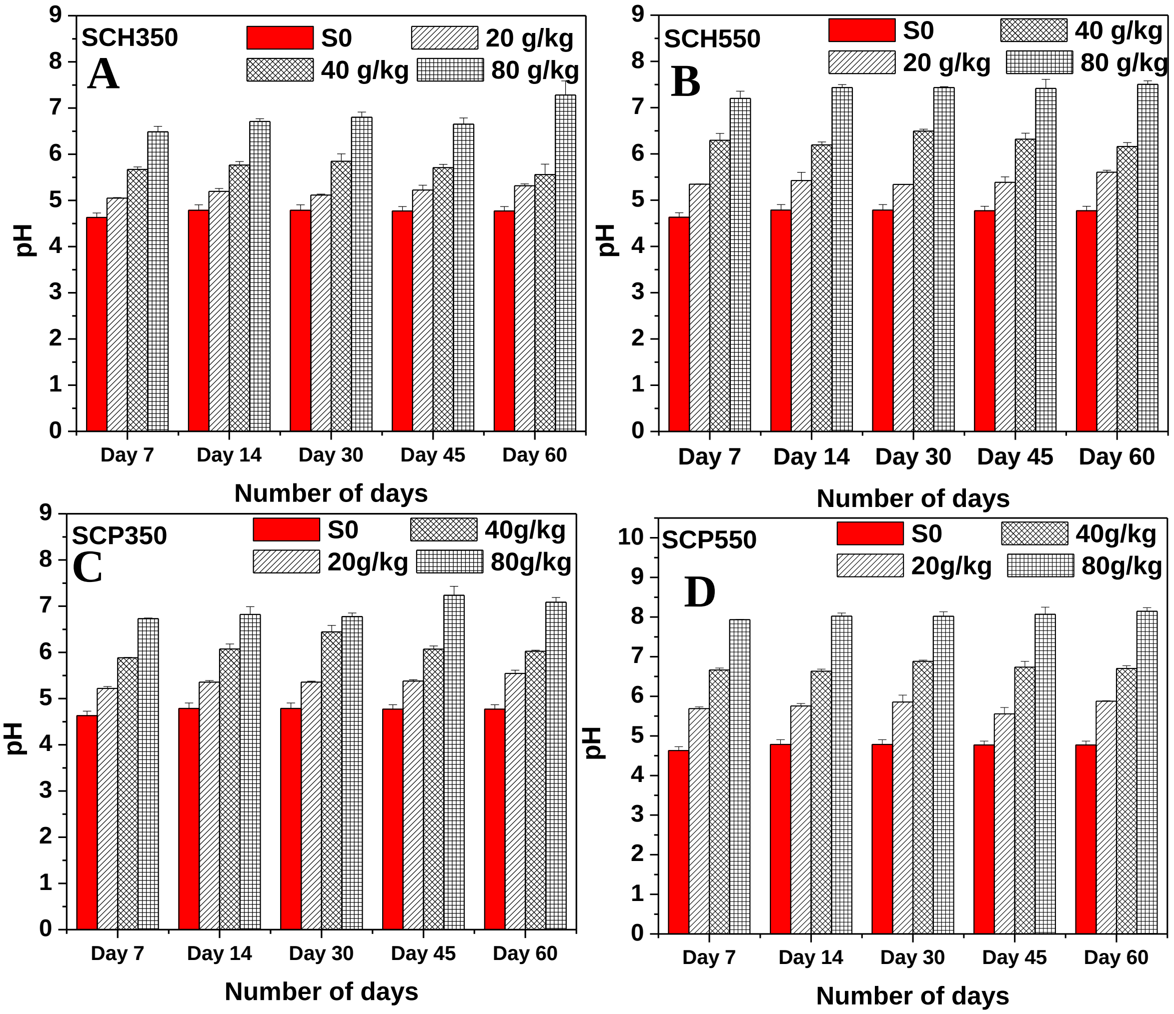


Figure 20*:* Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with respond soil pH

Furthermore, it should be noted that, after 60 days of incubation, the increase in soil pH with amendment rate (20, 40 and 80 g/kg) for each biochar were: for CH350; 0.46, 0.81, 2.51units, for CH550; 0.75, 1.41, 2.71units, for CP350; 0.68, 1.27, 2.32units and for CP550; 1.02, 1.95, and 3.3 units as compared with the control. Therefore, the liming effect was in the order CP550 > CH550 > CP350 > CH350. In the same way, studies on the impact of biochar on soil pH have previously been reported. Application of corn cob and switch grass at the rate of 52, 104, and

156 Mg ha^{-1} significantly increases soil pH by 0.73, 0.99, 1.36 units and 0.49, 0.74, and 0.91 units respectively [24]. Yuan and Xu [330] reported that biochar from leguminous plant caused a significant increase in soil pH as compared to non-leguminous plant, at the end of incubation, leguminous plant such as mungbean, peanut, soybean, faba bean, and pea increase soil pH by 0.83, 0.82, 0.70, 0.65 and 0.57 unit respectively and those from non-leguminous plant such as straw from canola, rice, corn, and wheat increase soil pH by 0.51, 0.39, 0.36, 0.32 and 0.25 unit with incubation rate of 1%. The increase in soil pH by these biochars can be due to the biochar alkalinity, $CaCO_{3(eq)\%}$ content, the presence of silicate, carbonate, and bicarbonate minerals, the presence of negatively charged phenolic, carboxyl and hydroxyl groups on biochar surfaces, acid-neutralizing capacity of the biochar. From biochar analysis, cocoa pod husk biochar had higher biochar alkalinity than coffee husk biochar at the same temperature (Table 8) which reacts with H^+ from the solution, reducing the H^+ ions concentration [331]. Moreover, the presence of more silicates, carbonates, and bicarbonates in CP550 than in CH550 as can be seen on the XRD spectrum makes it have a better liming potential value. The lower temperature produced biochars cause an increase in soil pH due to functional groups on the biochar such as $–COO^-$ and $–O^-$ which combines with H^+ and thereby removing it from soil solution [86]. Unlike other report has observed the decline of soil pH during the first 20 days of incubation [332] due to nitrification of NH_4^+-N, we observed a continuous increase from the first day to the 60th day. The continuous increase in pH may be due to a slow release of basic ions from the carbonates and bicarbonates [86] and also due to the buffering capacity of the biochar (Alkalinity of biochar in Figure 10) which can reabsorb the H^+ released during nitrification of NH_4^+-N. In addition, this positive correlation can be observed in works of Chintala and collaborators [24] and Yuan and Xu [330]. The former used corn corb and switch grass pyrolyze in a microwave at 650°C for 18 min while the latter used nine biochar types which were produced from leguminous and non-leguminous plants. From the study, analysis of variance showed the effect of amendment type and incubation time significantly varied ($P < 0.05$) the soil pH only at higher incubation rate for all four biochars. The effect of amendment rate and incubation time on pH had a significant effect ($P < 0.05$) for CH350, CH550, and CP350 and was not influence significantly ($P > 0.05$) by CP550. The increase in soil pH of acidic soils when incorporated with biochar limit metal toxicity and nutrients deficiencies, but also can lead to negative effect associated with excessively high pH on crop production [333].

3.2.2 Effect on soil electrical conductivity

Incorporation of all four biochars in soil significantly increased the soil EC ($P < 0.05$) at different incubation days as compared to control (Figure 21 A – D). After 7 days of incubation, 20, 40 and 80 g/kg of biochar amendments increased the electrical conductivity by 80.3, 160.3, and 252.0 units for CH350, 104.5, 207.0 and 294.5 units for CH550, 126.0, 266.0, 270.5 units for CP350 and finally 164.0, 292.0 then 352.5 units for CP550 respectively compared to control. This increase was in the order CP550 > CH550 > CP350 > CH350. From Day 7 to 14, the EC increased drastically for all four biochars before forming a plateau and the increase in soil EC for amendment rate of 80 g/kg for CP550 was more remarkable. After 60 days of incubation, the amended soils at 80 g/kg presented the highest EC (595.5, 629.8, 642.3, and 871.5 µS/cm for CH350, CH550, CP350, and CP550 respectively). The time of incubation of biochar at all soil-biochar amendment rates had a significant effect on the increase in soil EC ($p < 0.05$). Similar to these observations, Chintala and collaborators [24] observed a significant increase in soil EC and a stabilization of soil EC after 15 days of incubation. Moreover, previous work had indicated that an increase in soil EC is attributed to the alkalinity, $CaCO_3$ equivalence, ash content, and the amount of soluble salts in the incorporated biochar [76,314]. From the analysis of EC of biochar (Table 8), the increase in electrical conductivity of soil-biochar follows the same order as the abovementioned characteristic of the biochars.

The sharp increase in EC from the 14th day of incubation may be due to the dissolution of low solubility calcite in the biochar due to its reaction with H^+ in the acid soil to release calcium ions and the plateau form later may be due to the complete dissolution of the calcite. Furthermore, we can note that biochar produced from cocoa pod husk at 550 ºC increased EC more remarkably which can be attributed to the presence of sylvite, bicarbonate of potassium on XRD spectra of CP550. Analysis of variance showed that amendment type and amendment rate had a significant effect ($P < 0.05$) on soil EC from the 14th day of incubation to the 60th day. Also, amendment rate x incubation time, amendment type x incubation time had a significant effect ($P < 0.05$) on soil EC.

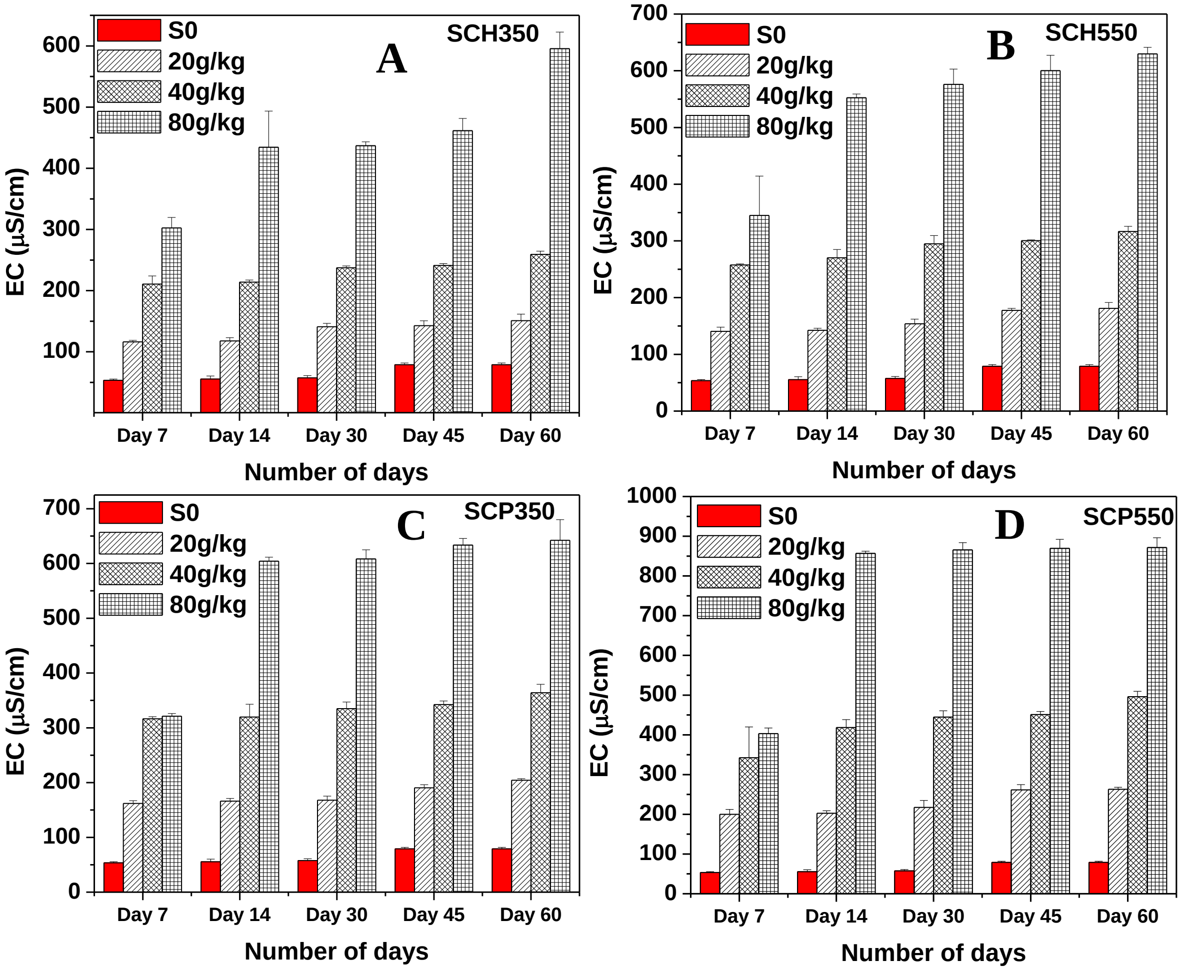


Figure 21: Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with respond soil electrical conductivity

3.2.3 Effect on available phosphorus

The quantity of available P in acidic soil significantly ($P < 0.05$) increased when amended with biochar (Figure 22). During the whole incubation period, a slight increase of available P was observed in the control acidic soil from 16.27 mg/kg after 7 days to 21.10 mg/kg after 60 days. This increase in available P could be due to P mineralization which occurs when dried soils are rewet [334]. After seven days of incubation of soil samples with different biochars, the amount of available P increased significantly ($P < 0.05$). Soil sample incubated at 20, 40 and 80 g/kg amendments increased the available P to 23.9%, 40.55 %, and 147.5 %. For CH350, 24.0 %, 36.0 %, 31.96 % for CH550, 37.0 %, 49.7 % and 167.2 % for CP350, and 33.3 %, 48.9 % and

181.2 % for CP550. The increase was in the order CP550 > CP350 > CH350 > CH550. Therefore, biochar produced from cocoa pods had a greater effect on the availability of P than those produced from coffee husk. A rise and fall in the amount of available P were observed with increasing incubation time. This rise and fall were dependent on the biochar type and amendment rate. Generally, soil incubated at 20 g/kg had a longer rising period for available P (averagely 45 days for all four biochars), then followed by an amendment rate of 40 g/kg whose available P rose with time up to the 30th day (except for CP550 = 14 days) and the shortest risen time was for amendment rate of 80 g/kg, which corresponded to 14 days (except for CH350 = 7 days). In summary, we can conclude that increasing the rate of biochar, release rapidly available P. With respect to control acid soil, the amendments rates 20, 40 and 80 g/kg increased the available P percentage was 51.9, 64.9 and 124.7 % for CH350, 49.5, 58.5 and 101.9% for CH550, 56.5, 78.9 and 135.1% for CP350, and finally; 59.5, 69.0 and 151.4% for CP550. On the other hand, the percentage decrease after 60 days of incubation compared to the maximum amount of available P release was for 20, 40 and 60 days was relatively little

Several works have asserted the inconsistency on the effect of biochar on soil P availability. This due to the manner in which biochar application affects the P cycle either directly or indirectly through various mechanisms such as biochar as a source of soluble P, biochar as a modifier of soil pH and ameliorator of P complexing metals (Al^{3+}, Fe^{3+}, Fe^{2+}), and biochar as a promoter of microbial activity, [31,31,335–337]. Dume and collaborators [338] observed an increase of about 84.3% of P availability after 2 months of incubation with coffee husk and corn cob biochar. Also, the application of poultry litter biochar increased water extractable P in acidic soil [339]. In this work, an increase in the availability of P from soil-biochar mixture could be as a result of direct supply of P from biochar and dissolution of inorganic P in the acid soil.

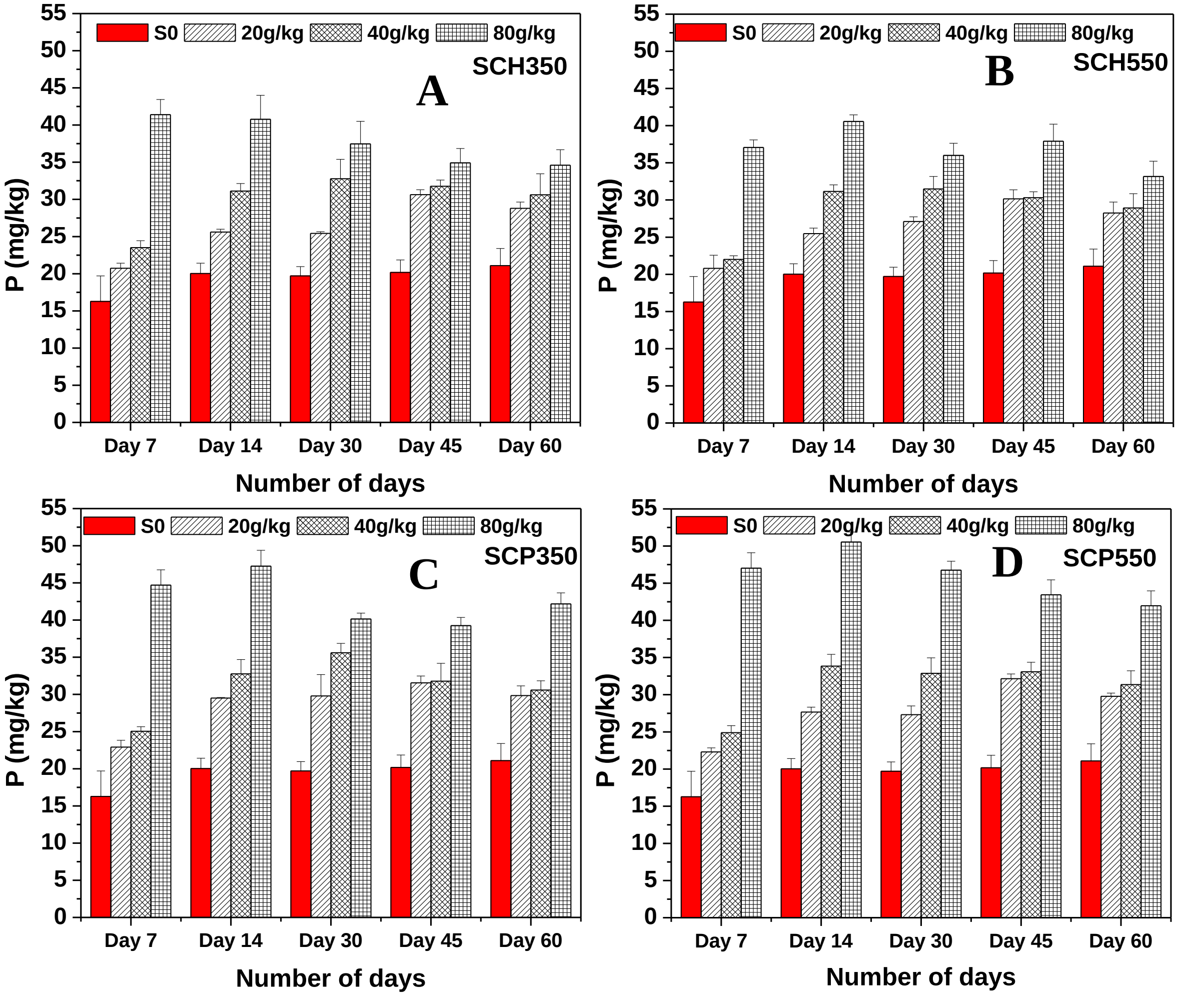


Figure 22: Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with respond on available P.

The second phase of incubation time shows a retention of available P after the increase as observed in the research work of Zwetsloot and collaborators [337], mixing wood biochar did not increase P availability. The reduction in available P could be explain by ash minerals from biochar precipitate P release in the soil solution phase [340]. Also, the increase in soil pH up to the alkaline medium and the high level $CaCO_3$ equivalent in biochar produced at higher temperature could cause the retention of P through the formation of Ca-P precipitates [339].

3.2.4 Effect on exchangeable acidity, Al and Fe

- ***Exchangeable acidity***

Results showing the effect of all four biochar on exchangeable acidity can be depicted on the Figure 23. Compared to control the application of biochar decreases drastically the exchangeable acidity ($P < 0.05$).

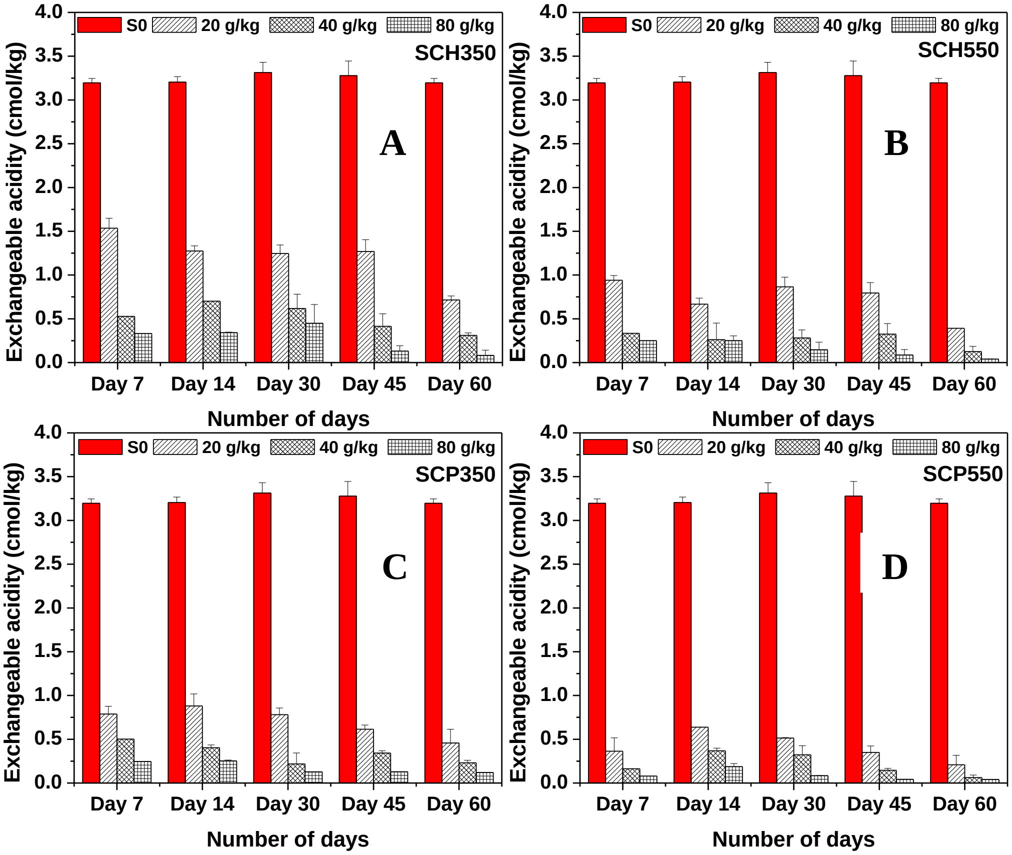


Figure 23: Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with respond on Exchangeable soil acidity.

All four biochars cause a progressive decrease in exchangeable acidity in the acid soil samples. After 45 days of incubation time, the amendments 20, 40, and 80 g/kg led to a decline was significantly higher for CP550 (89.18%, 95.52 % and 98.7 % respectively), followed by CH550 (75.45%, 89.96% and 97.30% respectively), then CP350 (81.03%, 89.43 % and 96.08 % respectively) and finally CH350 treatment (60.82 %, 87.20 % and 95.00% respectively). Thus the effect of the different biochars on exchangeable acidity is in the order CP550 > CH550 > CP350 > CH350. There was a significant difference ($p < 0.05$) on the effect of soil acidity with application rate of the four biochars, but on the 60th day, application rate had no significant difference ($P > 0.05$) on exchangeable acidity. The analysis of the variance showed the effect of amendment type and incubation time significantly varied ($P < 0.05$) the soil exchangeable acidity. The amendment rate, and incubation time for CH350, CH550, and CP350 had a significant effect on the variation of soil exchangeable acicidity ($p < 0.05$) while for CP550 there was no significant difference on parameter under study ($p > 0.05$).

- ***Exchangeable Al and Fe***

Acid soil treated with all four biochars decrease drastically exchangeable Al and Fe significantly ($P < 0.05$). The decrease was very rapid after 7 days of incubation then decreased slowly to its minimum value.

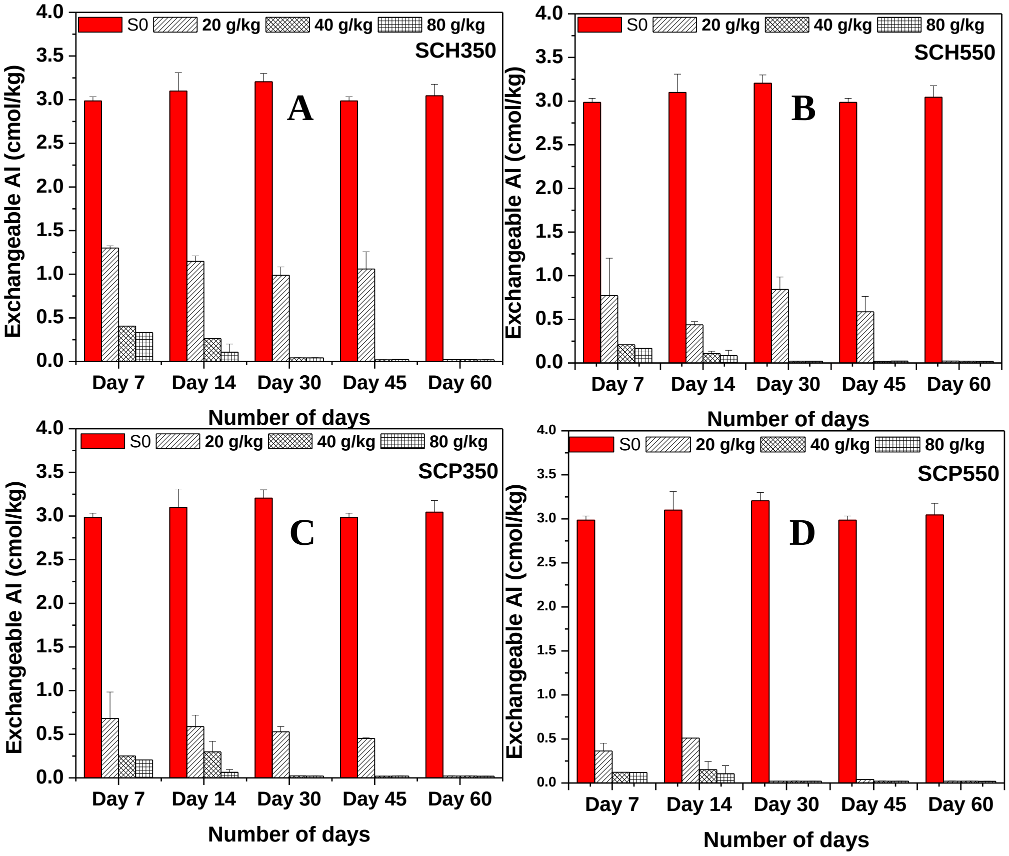


Figure 24: Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with respond on Exchangeable Aluminium

As can be depicted from Figure 24 and Figure 25, the order of alleviation of Al and Fe by the different biochar treatment is CP550 > CH550 > CP350 > CH350. Incubation time significantly varied ($p < 0.05$) with exchangeable Al and Fe indifferently with the biochar type and amendment rate, with exception only to CP550 biochar at amendment rate of 40 and 80 g/kg which had no significant difference ($p > 0.05$) in exchangeable Al and Fe with incubation time. Amendment rate had a significant ($p < 0.05$) difference on exchangeable Al for each incubation days. From the study, analysis of variance showed that the effect of amendment type and incubation time significantly varied ($p < 0.05$) the soil exchangeable Al and Fe. The amendment rate, and incubation time for CH350, CH550, and CP350 had a significant effect on the variation of soil exchangeable acicidity ($p < 0.05$) while for CP550 there was no significant difference on parameter under study ($p > 0.05$).

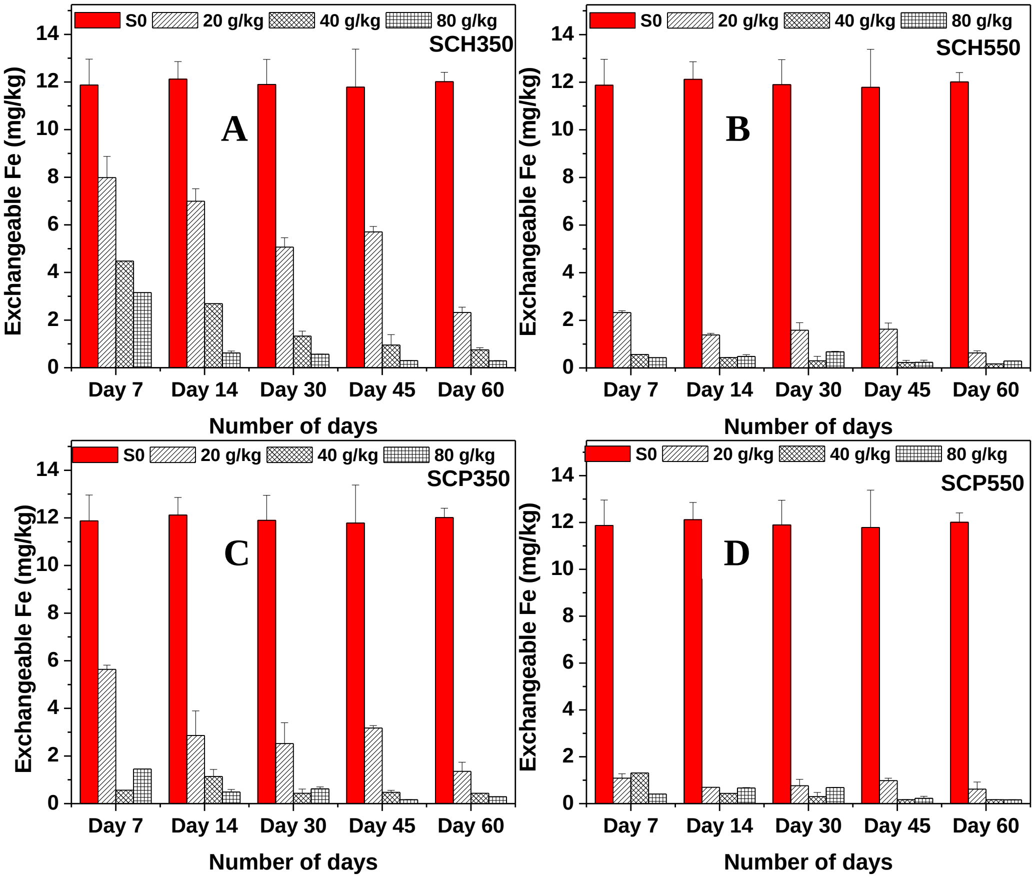


Figure 25: Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with respond Exchangeable Iron

The major ions concern in this exchangeable medium are the H^+, Al^{3+}, Fe^{2+}, and $Fe^{,3+}$. The mechanism involves precipitation of the metallic ions by alkaline oxides, carbonates, and silicates in the biochar, complexation with organic functional groups (e.g. –O, -OH, COOH) found on the biochar surface [341]. From the characteristic of the biochar listed in Table 8, the removal of these ions from the soil solution is predictable. The order of effect of biochar type on the reduction of exchangeable Al and Fe based on the biochar properties shows that CP550 had the highest liming equivalence, acid-neutralizing capacity, and biochar alkalinity and contain many basic minerals (Figure 16) which can relate to its ability to have a greater reduction in exchangeable acidity, Al and Fe.

Recent works on the application of biochar into soils and its effect on soil acidity and exchangeable Al and Fe asserted the same observation [24,338,342].

3.2.5 Effect on soil organic carbon

All four biochar amended soils had significantly higher soil organic carbon ($p < 0.05$) than the control throughout the incubation time (Figure 26). It is observed that for biochars produced at a lower temperature, the increase in soil organic carbon was proportional to the biochar application rate. After 30 days of incubation, the highest soil organic carbon was observed. In the soil amended with biochar at 20, 40 and 80 g/kg, the increase in soil organic carbon as compared to the control were 2.7, 2.6, and 3.2-fold for CH350, 1.99, 1.97, and 2.1 for CH550, 2.5, 2.6, and 3.6 fold for CP350 and lastly 2.1, 2.4 and 3.1 for CP550 respectively. Also, the increase in soil organic carbon was more pronounced when amended with cocoa pod husk biochar than coffee husk biochar. From the 30th day to the 60th day of incubation, a decrease in soil organic carbon was observed. The decrease was more pronounce in biochar produced at lower temperature as compared to those produced at higher temperature. An increase or a decrease in soil organic carbon in soils can be due to negative or positive priming effect of biochar with incubation time. A negative priming effect causes an increase in soil organic carbon which is due to the presence of recalcitrant carbon [343] and decrease in the mineralization of the soil carbon. The decrease in mineralization could be due to several reasons such as (i) sorption of labile soil organic matter onto the biochar pores [344], (ii) a very short-term inhibitory effect of microbial activity of biochar–associated volatile organic compounds [345]; and/or (iii) a transient shift to a more labile substrate in biochar, relative to those in the low-C clayey soil [346].

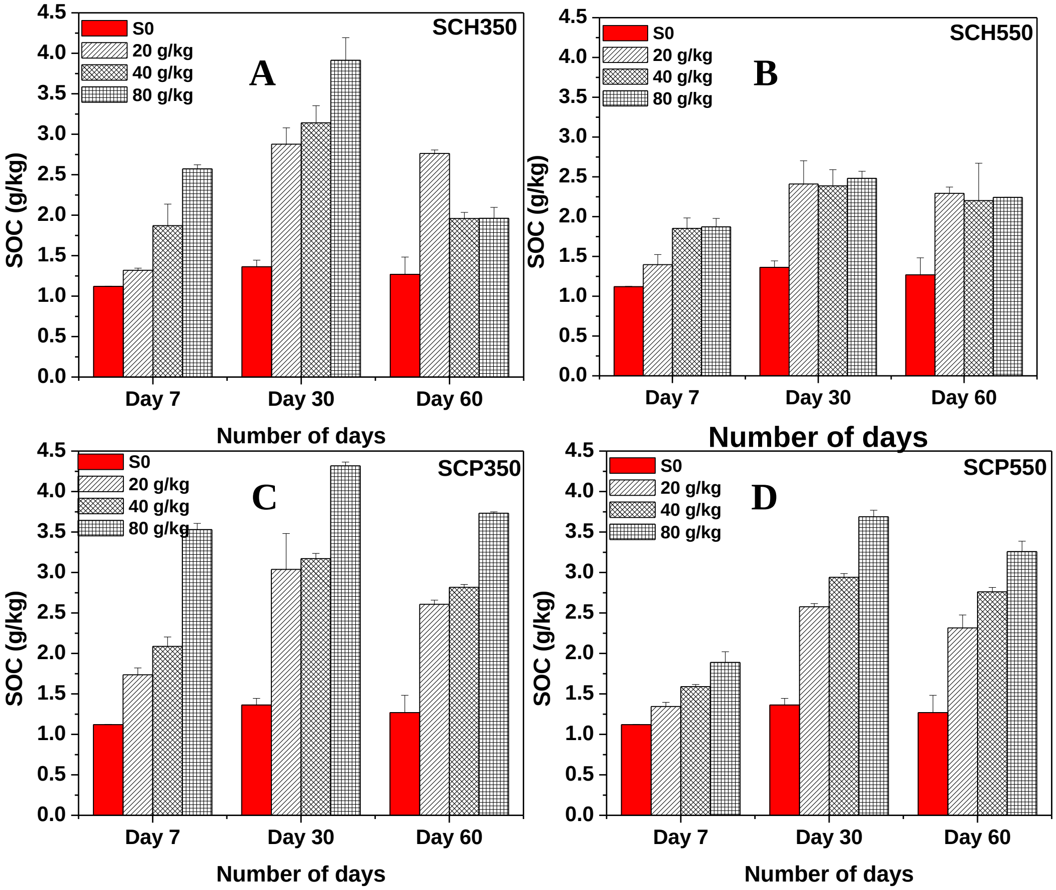


Figure 26: Effect of (A) CH350, (B) CH550, (C) CP350 and (D) CP550 biochar application rate and incubation time on acidic soil with soil organic carbon.

Generally, biochar produced at higher temperature has greater pores and therefore thus can have greater sorption facilities which may fulfil the sorption hypothesis thus causing a greater increase in soil organic carbon after 30 days of incubation. The positive priming effect which causes a decrease in soil organic carbon after 30 days may be due to remains of labile organic material remaining in the biochar [347] which in turn activate soil microorganisms. Previous research evaluating the stability of biochar due to the soil organic content has been studied with either a decrease or increase [343,344,347].

3.2.6 Analysis of Pearson correlation coefficients for the relationships between soil pH, soil EC, available P, Exchangeable Acidity, Aluminium and Iron.

From Table 12, Pearson correlation reveals that, increase in soil pH had a positive significant correlation ($p < 0.05$) when incorporated with CH350, CH550 and CP350 at 20, 40, and 80 g/kg with incubation time, but for CP550, positive significant correlation ($p < 0.05$) occurred only at high amendment rate ($r = 0.938$). Also, there is a positive significant correlation between soil pH and Soil EC and available P for all four biochars at different amendment rate. Moreover, there is a significant negative correlation of soil pH with Exchangeable acidity, Al and Fe for all four biochars amendment rates. Soil EC had a positive significant ($p < 0.05$) correlation for all four biochar, irrespective of the amendment rates and incubation days. Furthermore, Soil EC had a positive significant correlation with available P, except at the highest dosage, whereas, negative significant correlations between soil EC and exchangeable acidity, Al and Fe in all incubation systems were obtained. Available P had a significant positive correlation coefficient with number of incubation days for all four biochars amended at 20 and 40 g/kg. On the contrary, a negative significant correlation was observed at higher doses. In the same line, available P had a significant negative correlation with exchangeable acidity, Al, and Fe for all four biochar at 20 and 40 g/kg dosage was computed. Meanwhile at 80 g/kg, the correlation is significantly positive. In the case of exchangeable Al and Fe, all four biochar and their amendment rate had significant ($p < 0.05$) negative correlation with incubation time. A positive correlation of soil pH with incubation time is due to the slow release or dissolution of calcite from the biochar and the buffer properties of the biochar, thus causing a progressive increase in soil pH and a negative correlation with exchangeable acidity, Al, and Fe due to the precipitation of these exchangeable's. Similar to previous studies [332], biochar amendments significantly improve soil pH and decreases exchangeable Al and acidity. A positive correlation in soil ECs with number of days is linked to slow dissolution of the basic compounds in the biochar to release soluble ions responsible for the soil EC. The positive correlation with available P may be due to the addition of P from the biochar, thus enhancing P. whereas the negative correlation at 80 g/kg may be due to the saturation of the soil solution with soluble basic cations and available P which leads to the precipitation of phosphate. The antagonistic effect of available P with Ex Ac, Al and Fe is well known. It is due to the exchange reaction of Al and Fe with the alkaline from biochar and the functional groups (-O- and –COO-) with the biochar and liberating phosphate and also the provision of P into the soil solution as biochar plays the role of P provider.

Table 12: Pearson's correlation coefficients for the relationships between incubation time (Days), soil pH (pH), soil EC (EC), available P (Avail P), exchangeable Acidity (Ex Ac), exchangeable Aluminium (Ex Al) and exchangeable Iron (Ex Fe) on the amended soils at different rates.

SCH350

		Days	pH	EC	Avail P	Ex Ac	Ex Al	Ex Fe
20 g/kg	Days	1	**0.841**	**0.954**	**0.847**	**-0.859**	**-0.841**	**-0.923**
	pH		1	0.670	**0.841**	**-0.571**	-0.589	**-0.789**
	EC			1	**0.773**	**-0.766**	**-0.753**	**-0.907**
	Avail P				1	-0.633	-0.519	-0.659
40 g/kg	Days	1	**0.831**	**0.982**	0.547	**-0.801**	**-0.882**	**-0.893**
	pH		1	**0.803**	0.386	**-0.748**	**-0.597**	**-0.850**
	EC			1	0.555	**-0.759**	**-0.900**	**-0.894**
	Avail P				1	0.048	**-0.824**	**-0.859**
80 g/kg	Days	1	**0.802**	**0.902**	**-0.973**	**-0.764**	**-0.787**	**-0.705**
	pH		1	**0.927**	-0.661	**-0.738**	**-0.843**	**-0.603**
	EC			1	**-0.809**	-0.646	**-0.837**	**-0.821**
	Avail P				1	**0.704**	**0.809**	**0.712**

SCH550

	Days	Days	pH	EC	Avail P	Ex Ac	Ex Al	Ex Fe
20 g/kg		1	**0.702**	**0.974**	**0.828**	**-0.693**	**-0.649**	**-0.781**
	pH		1	0.615	0.370	**-0.978**	**-0.981**	**-0.887**
	EC			1	0.831	-0.593	-0.586	-0.658
	Avail P				1	-0.462	-0.384	-0.650
40 g/kg	Days	1	**0.737**	**0.978**	0.426	-0.659	**-0.833**	**-0.966**
	pH		1	**0.833**	0.156	-0.546	**-0.780**	**-0.837**
	EC			1	0.554	-0.649	**-0.915**	**-0.989**
	Avail P				1	-0.276	**-0.818**	-0.633
80 g/kg	Days	1	**0.738**	**0.798**	-0.676	**-0.988**	**-0.826**	-0.522
	pH		1	**0.976**	-0.247	-0.666	**-0.896**	-0.100
	EC			1	-0.239	**-0.749**	**-0.956**	-0.191
	Avail P				1	0.713	0.361	0.156

SCP350

20 g/kg	Days	1	**0.899**	**0.958**	0.675	**-0.921**	**-0.912**	**-0.772**
	pH		1	**0.877**	0.692	**-0.775**	**-0.951**	**-0.926**
	EC			1	0.562	**-0.958**	**-0.925**	-0.669
	Avail P				1	-0.354	-0.476	**-0.822**
40 g/kg	Days	1	**0.852**	**0.986**	0.316	**-0.765**	**-0.848**	-0.560
	pH		1	**0.823**	0.378	**-0.710**	-0.484	**-0.885**
	EC			1	0.258	**-0.776**	**-0.817**	-0.577
	Avail P				1	**-0.736**	-0.441	0.080
80 g/kg	Days	1	**0.814**	**0.706**	**-0.648**	**-0.877**	**-0.749**	**-0.762**
	pH		1	0.429	-0.519	-0.594	-0.431	-0.623
	EC			1	-0.390	-0.642	**-0.983**	**-0.966**
	Avail P				1	0.901	0.534	0.419

SCP550

20 g/kg	Days	1	0.194	0.955	0.794	-0.663	**-0.818**	-0.448
	pH		1	-0.010	-0.165	0.010	-0.157	**-0.769**
	EC			1	0.828	-0.714	**-0.770**	-0.212
	Avail P				1	-0.202	-0.563	-0.384
40 g/kg	Days	1	0.264	0.910	0.427	-0.611	**-0.838**	**-0.774**
	pH		1	0.829	0.297	-0.593	**-0.701**	**-0.877**
	EC			1	0.722	-0.247	**-0.722**	**-0.939**
	Avail P				1	0.406	-0.314	**-0.901**
80 g/kg	Days	1	0.939	0.640	-0.872	-0.670	**-0.876**	-0.679
	pH		1	0.772	-0.677	-0.382	**-0.751**	-0.545
	EC			1	-0.207	0.043	**-0.705**	0.028
	Avail P				1	**0.932**	**0.735**	**0.874**

*** Coefficients that are significant ($p < 0.05$) are shown in bold text.**

3.2.7 Partial conclusion

The objective of this study was to evaluate the effects of biochar rate and incubation time on soil chemical properties and the following main findings where obtained: (i) increase in biochar rate and incubation time for all four biochar, effectively alleviate the soil acidity by yielding an increase in soil pH, soil EC and a drastic drop in exchangeable acidity, exchangeable Al and Fe. CP550 caused the greatest increase in soil pH; (ii) the fertility aspect of the biochar was demonstrated with the increase in available P upon addition of biochar. Available P rises with biochar rate and incubation time. It was observed a readsorption of P at higher dosage with rising incubation time; (iv) biochar amendment rised soil organic carbon. Rise and drop in soil organic carbon was more pronounced with biochar produced at lower temperature. The effect of biochar on these soil chemical properties was mainly due to the intrinsic chemical properties of the biochar such as biochar alkalinity, acid-neutralising capacity, $CaCO_3$eq(%), presence of basic inorganic minerals, presence of complexing functional groups and P availability. Thus clear knowledge liming and fertilizing properties of biochar and its effect on soil properties is useful. Hence, biochar can play the dual role of a liming agent and a source of P fertilizer nutrients. Implementing these types of studies with different biochar obtained from these localities and testing its beneficial agricultural amendments value on their soils, will help to design biochars for farmers in these localities.

3.3 Phosphorus fixation and release in acid soils amended with biochar

The phosphorus sorption study is aimed at determining the amount of P that the soil, soil-biochar adsorb in solutions with different concentration of P at equilibrium. The adsorption data were fitted in Langmuir and Freundlich isotherms in other to elucidate the mechanism of adsorption and estimate the adsorption maximum, adsorption capacity and adsorption energies.

3.3.1 Brief discussion on the chemical characterisation of the amended soil samples used for the study

This section discusses briefly the characterization of the selected amended soil samples used for phosphorus fixation and release study. This brief discussion of the physicochemical properties of the amended soil samples will help us to better understand the trend and mechanism of sorption and desorption of phosphorus in the section 4.3.3.

From Table 13, after 7 days of incubation, CH350, CH550, CP350 and CP550 at rate of 0, 20, 40 and 80 g/kg raised the soil pH from 4.70 to 5.05, 5.67 and 6.49; 5.35, 6.30 and 6.49; 5.22, 5.89 and 6.73; 5.69, 6.67 and 7.94 respectively. Also, after 60 days of incubation, CH350, CH550, CP350 and CP550 at rate of 20, 40 and 80 g/kg raised the soil pH from 4.70 to 5.32, 5.56 and 7.28; 5.61, 6.16, 7.51; 5.54, 6.03 and 7.09; 5.88, 6.70 and 8.15 respectively. It is observed an increment in soil pH from day 7 to 60. Moreover, the pH of soil-biochar mixture increased with rising pyrolysis temperature and with biochar application rate with cocoa pod husk having the greater impact compared to coffee husk. The application of biochar on soil had a significant effect ($p<0.05$) in elevating the soil pH. Soil pH rises due to addition of biochar, attributed to higher $CaCO_{3(eq)\%}$ content and acid-neutralising capacity of the biochar. Also, due to the presence of silicate, carbonate, and bicarbonate minerals and negatively charged phenolic, carboxyl and hydroxyl groups on biochar surfaces. At higher temperature, the silicates, carbonates, and bicarbonates are mostly the cause of elevation in pH while at low temperature produced biochar, the basic functional groups on the biochar such as –COO- and –O- are responsible [86].

An increase in EC was observed and higher in soil-biochar mixed with cocoa pod husk than coffee husk for the same amendment rate and pyrolysis temperature. Details from Table 13 indicates that, after 7 days of incubation at 20, 40 and 80 g/kg amendments rate increase in soil

EC to 116.25, 210.75 and 302.50 µScm^{-1} for CH350, 140.50, 257.50 and 345.00 µS.cm^{-1} for CH550, 162.00, 316.50, 321.25 µS.cm^{-1} for CP350 and finally 200.00, 342.50 then 403.00 µS.cm^{-1} for CP550 respectively as compare to control. This increase was in the order CP550 > CH550 > CP350 > CH350. Moreover, from 7 to 60 days of incubation, CH350, CH550, CP350 and CP550 at rate of 20, 40 and 80 g/kg raised the soil EC to 151.00, 364.00 and 595.50; 181.00, 316.75, 629.75; 204.25, 364.00 and 642.258.15; 263.00, 496.00 and 871.50 respectively. The sharp increase in electrical conductivity from the 7th to the 60th day of incubation is due to the dissolution of kalicinite and calcite by reaction with H^+ in the acid soil solution to release calcium and potassium ions.

Application of biochar on acid soil samples resulted in an increase in available P as compared to control. After seven days of incubation, CH350, CH550, CP350 and CP550 at amendment rate of 20, 40 and 80 g/kg raise the available P by 23.9 %, 40.55 %, and 147.5 % ; 24.0 %, 36.0 %, 31.96 %; 37.0 %, 49.7 % and 167.2 % and 33.3 %, 48.9 % and 181.2 % respectively. The increase was in the order CP550 > CP350 > CH350 > CH550. From 7 to 60 days of incubation, at amendment rate of 20 and 40 g/kg, a rise in available P was observed; which can be attributed to, biochar as a source of soluble P, it reaction with complexing metals (Al^{3+}, $Fe^{3+,2+}$), releasing P and promotion of microbial activity. Whereas, at 80 g/kg, a decreases in available P was observed which can be due to the formation of Ca-P precipitates attributed to the presence of $CaCO_3$ found in high amount of ash minerals in the biochar [339,340].

A drastic drop in exchangeable acidity, exchangeable Al and Fe was observed with incubation time (Table 13). With respect to exchangeable acidity, after 60 days of incubation the amendment rate of 20, 40 and 80 g/kg led to a significant decrease which was higher for CP550 (93.42%, 98.12%, and 98.75%), followed by CH550 (87.77%, 96.24% and 98.74%), then CP350 (85.58%, 92.79% and 96.24%) and finally CH350 treatment (77.43%, 90.28% and 97.49%). After 7 days of incubation, the drop in exchangeable acidity, exchangeable Al and Fe by the application of biochar was in the order CP550 > CH550 > CP350 > CH350. Increase in amendment rate, had a significant drop in exchangeable Acidity, Al and Fe in the acid soil sample. The cause of reduction can be attributed to the precipitation of the metallic ions by alkaline oxides, carbonates and silicates in the biochar, complexation with organic functional groups [341]. Recent works of the application of biochar into soils and its effect on soil acidity and exchangeable Al and Fe asserted the same observation [24,338].

Rise in soil organic carbon in soil amended with biochar was observed as compared to the control (Table 13). The rise in soil organic carbon increased with incubation time and amendment rate. Elevation in the amount of soil organic carbon was more pronounced when amended with cocoa pod husk than coffee husk biochar and for biochar produced at 350 °C than those produced at 550 °C. An inflation in soil organic carbon is due to the presence of recalcitrant carbon [343] and decrease in the mineralization of the soil carbon due to sorption of labile soil organic matter onto the biochar particles [344] and/or a very short-term inhibitory effect of microbial activity of biochar–associated volatile organic compounds [345].

Table 13: Physicochemical properties of soil and soil-biochar mixture after amending for 7 and 60 days

Days	Soil-biochar mixture	Amendment rate	pH	EC (µS/cm)	Avai. P (mg/kg)	Ex Acidity (cmol(H^+)/kg	Ex Al (mg/kg)	Ex Fe (mg/kg)	SOC (mg/kg)
7	S0	0	4.70±0.01	53.50±2.12	16.27±3.43	3.20±0.05	2.985±0.048	11.87±1.09	1.12±0.01
	SCH350	20	5.05±0.01	116.25±2.50	20.73±0.69	1.54±0.11	1.301±0.025	7.99±0.89	1.32±0.02
		40	5.67±0.06	210.75±13.33	23.51±0.93	0.53±0.09	0.406±0.058	4.49±0.21	1.87±0.27
		80	6.49±0.12	302.50±17.08	41.41±2.03	0.33±0.05	0.332±0.023	3.16±0.25	2.57±0.05
	SCH550	20	5.35±0.01	140.50±7.55	20.81±1.77	0.94±0.05	0.771±0.429	2.33±0.08	1.40±0.13
		40	6.30±0.15	257.50±2.08	22.02±0.47	0.33±0.02	0.209±0.045	0.56±0.31	1.85±0.13
		80	7.20±0.16	345.00±19.24	37.06±1.03	0.25±0.02	0.168±0.028	0.43±0.27	1.87±0.11
	SCP350	20	5.22±0.04	162.00±4.97	22.91±0.91	0.79±0.08	0.682±0.302	5.64±0.18	1.74±0.09
		40	5.89±0.01	316.50±3.87	25.04±0.62	0.50±0.01	0.251±0.023	0.56±0.45	2.09±0.12
		80	6.73±0.01	321.25±4.79	44.71±2.05	0.25±0.01	0.205±0.035	1.45±0.56	3.53±0.08
	SCP550	20	5.69±0.04	200.00±12.33	22.30±0.54	0.36±0.05	0.363±0.089	1.08±0.19	1.34±0.05
		40	6.67±0.05	342.50±77.31	24.90±0.92	0.16±0.01	0.122±0.025	1.31±0.35	1.59±0.03
		80	7.94±0.01	403.00±14.31	47.04±2.06	0.18 ±0.02	0.119±0.048	0.41±0.89	1.89±0.13
60	S0	0	4.86±0.01	79.00±2.83	21.10±2.30	3.19±0.05	3.044±0.132	12.01±0.40	1.27±0.21
	SCH350	20	5.32±0.04	151.00±10.68	28.80±0.84	0.72±0.05	0.0220±0.0004	2.32±0.23	2.76±0.04
		40	5.56±0.23	259.25±5.32	30.62±2.83	0.31±0.03	0.0210±0.0008	0.75±0.09	1.96±0.08
		80	7.28±0.31	595.50±16.99	34.59±2.09	0.08±0.02	0.0200±0.0005	0.29±0.01	1.96±0.14
	SCH550	20	5.61±0.04	181.00±10.42	28.26±1.45	0.39±0.01	0.0220±0.0003	0.63±0.09	2.29±0.08
		40	6.16±0.08	316.75±8.96	28.93±1.92	0.12±0.01	0.0210±0.0002	0.17±0.01	2.20±0.47
		80	7.51±0.08	629.75±11.61	33.17±2.05	0.04±0.01	0.0200±0.0001	0.29±0.01	2.24±0.01
	SCP350	20	5.54±0.07	204.25±2.97	29.85±1.31	0.46±0.05	0.0210±0.001	1.36±0.38	2.61±0.05
		40	6.03±0.02	364.00±15.38	30.59±1.24	0.23±0.03	0.0210±0.0003	0.43±0.06	2.82±0.04
		80	7.09±0.10	642.25±17.74	42.19±1.49	0.12±0.01	0.0200±0.0001	0.29±0.01	3.73±0.02
	SCP550	20	5.88±0.01	263.00±4.90	29.78±0.44	0.21±0.01	0.0210±0.001	0.62±0.30	2.32±0.16
		40	6.70±0.07	496.00±13.44	31.36±1.86	0.06±0.03	0.0210±0.0001	0.17±0.06	2.76±0.05
		80	8.15±0.09	871.50±14.61	41.97±2.00	0.04±0.01	0.0200±0.0002	0.17±0.01	3.26±0.13

3.3.2 Point of zero charge analysis of soil and soil biochar mixture

The pH of point of zero charge is the pH value for which the net charge due to sorbed ions, other than H^+ and OH^- is equal to zero [250]. Figure 27 shows results of the determination of the pH of point of zero charge. It is observed that biochar type amendments to soil increases the pH at point of zero charge (pH_{PZC}) as compare to the control in the order SCP550 > SCH550 > SCP350 > SCH350. The increment in pH_{PZC} to basic pH values increased with amendment rate for a constant incubation period. The increment in pH_{PZC} after 7 days of incubation for amendment rates 20, 40 and 80 g/kg was in the order 0.44, 0.57 and 1.68 for SCH350, 0.55, 1.02 and 2.01 for SCP350, 0.50, 1.0 and 1.98 for SCH550 and 0.68, 1.76 and 2.32 for SCP550. These same increments were observe for soil-biochar incubated for 60 days with increase in amendment rate in the order 0.78, 0.98 and 2.19 for SCH350, 0.97, 1.55 and 2.32 for SCP350, 0.87, 1.55 and 2.26 for SCH550 and finally 1.09, 1.81 and 2.76 for SCP550. Comparing pH_{PZC} for all biochar type amendments and same incubation rate, there was a rise in pH_{PZC} from 7 to 60 days of incubation. Research has demonstrated that when pH is higher than the pH_{PZC} of a variable charge soil, the soil possesses a net negative charge on the surface and the potential of the adsorption plane are negative [348].

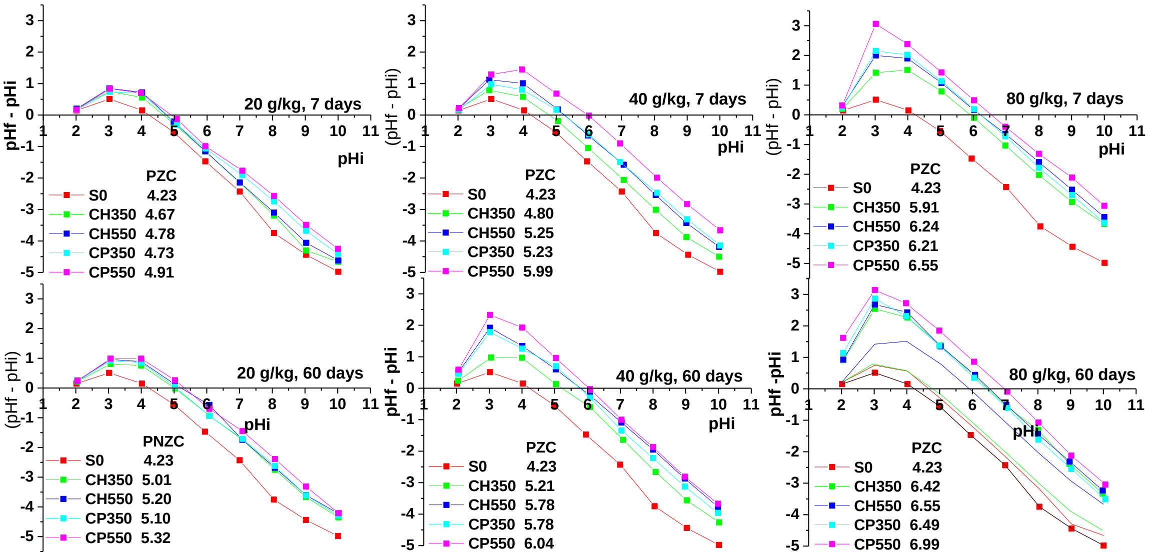


Figure 27: Plots of ΔpH vs pH_i for the determination of point of zero charge for amended soil sample at 20, 40 and 80 g/kg incubated for 60 days

In this light, we can estimate that adding biochar to soil considerably varied the surface charges of the soil resulting in the pH_{PZC} greater than the pH_{PZC} of the unadmended soil. Thus moving towards basic pH, one can expect soil-biochar mixture having a more and more negatively charged surface. This can be attributed to the presence of $–COO^-$ and $–O^-$ from the biochar and thus may repel negative ions.

3.3.3 Phosphorus sorption on soil and soil-biochar mixture

- ***Adsorption of phosphorus on soil***

Figure 28 represents the sorption curve for the adsorption of P onto soil incubated for 7 and 60 days. A rapid increase in the adsorption capacities of both soil samples are observed (due to incomplete occupation of adsorption sites), followed by a gradual slowdown for greater concentrations, until the formation of a plateau indicating a more or less saturation of the soil samples. This implies that the vacant adsorption sites for P declines as the concentration of the adsorbate rises [349] as the result of high affinity of the soil to P at low concentrations [245].

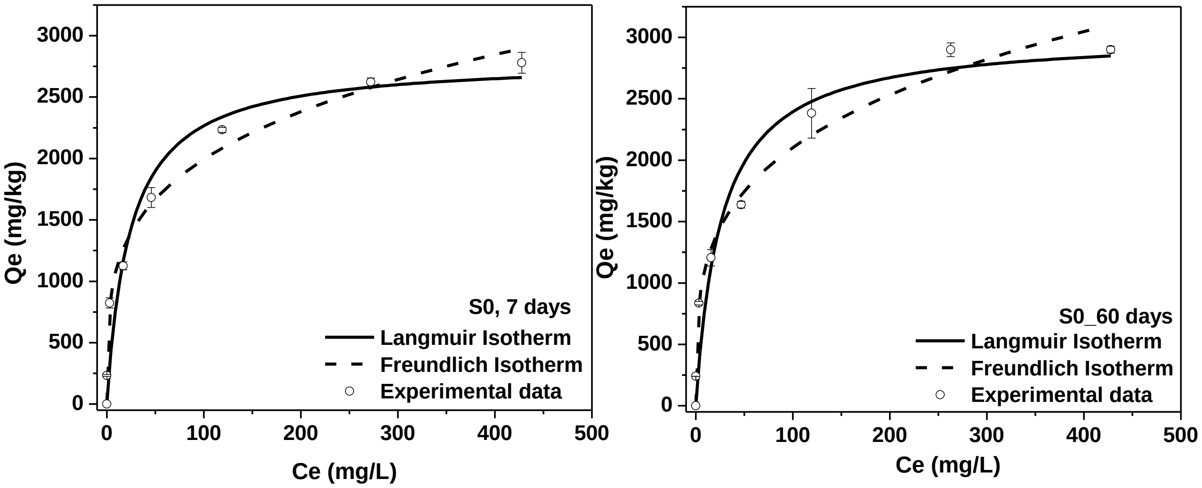


Figure 28: Langmuir and Freundlich phosphorus sorption isotherms of soil samples incubated for 7 and 60 days

For a more systematic study, the experimental data were interpreted using Langmuir and Freundlich isotherms and the obtained parameters, presented in Table 14. The experimental data of the sorption of P on soils samples fits into the two models ($R^2 > 0.9$) suggesting that the P adsorption is controlled by both Langmuir and Freundlich adsorption mechanisms.

Table 14: Langmuir and Freundlich parameters for unamended soil (S0)

Material	Incubation days	Langmuir			Freundlich		
		K_L (L/kg)	Q_{max} (mg/kg)	R^2	$\frac{1}{n}$	K_F (mg/kg)	R^2
S0	**7**	0.0418	2808.97	0.921	0.2570	610.15	0.986
S0	**60**	0.0359	3047.82	0.918	0.2671	613.33	0.979

This result indicated that the P adsorption could be governed by multiple mechanisms. Adsorption of P on Cameroonian acid soil had let to different conclusion as of the best fit isotherms. Previous work on the fixation of P on soil of the Eastern flank of Mount Cameroon displayed a best fit with Freundlich model even though both isotherms had a coefficient of determination greater than 0.9 [6]. Comparing the P sorption maximum obtained from Langmuir isotherm of the unamended soil (i.e. amendment at 0 g/kg of biochar) incubated for 7 and 60 days, there is a slight increase in Q_{max} and a decline K_L of P with increase in incubation days. We can suggest that, when dry soils are rewet, P mineralisation occurs causing P more available to the soil solution [334], thus resulting in a rise in Q_{max}. Moreover, the P sorption maximum values were higher than those obtained from experimental data, indicating that adsorption sites were not all occupied by P with similar results obtain by Njoyim and collaborators [267]. Also, a decline in binding energy is observed which may indicate a weak attachment of P on the soil surface of S0 after 60 days of incubation. From the Freundlich isotherm parameters, the adsorption capacities and sorption intensity were quite similar. A slight increase in sorption intensity with the soil sample with increasing number of incubation days (0.2570 for S0, 7 days and 0.2671 for S0, 60 days) may tend to prove that S0 at 60 days of incubation have a higher affinity to P adsorption.

- **Adsorption of phosphorus on soil-biochar**

Langmuir Isotherm Model

Figure 28, 29, 30 and 31, represents the graph with experimental data, simulated Langmuir curve for the adsorption of P onto soil amended with biochar produced from coffee husk and cocoa pod husk at 350 °C and 550 °C incubated for 7 and 60 days at room temperature. Typical isotherms profile curves and plotted data were observed as in other works [29,32]. From these Figures, we can observe that the plateaus of the amended soil samples were lower as compare to the control for all four biochar and irrespective of the incubation periods. This indicates that the adsorption capacities and activity of the adsorption sites were reduced. A logical explanation can be due to P release form biochar were sorbed to the soil surface and filled sorption sites, some of which are irreversible [350]. This situation leaves fewer available P sorption sites, reducing the total capacity for the sorption of P from external sources. Thus this study illustrates that biochar can reduce the soil's P-fixing potential. From figure 29, 30, 31 and 32, we observed that, the level of the plateau for all the four biochar declines with increase amendment rate from 20 to 80 g/kg, thus indicating a reduction in adsorption capacities with increase amendment rate. From the Langmuir isotherm parameters, P sorption maximum declines with increasing amendment rate for all four biochar type. For example, Q_{max} are 2266.50, 2047.84 and 1822.81 mg/kg for amendments with CH350 and 2121.84, 2031.83 and 1903.78 mg/kg for amendments with CP350 at amendment rate of 20, 40 and 80 g/kg for 7 days respectively. Studies have shown that adding biochar reduces sorption maximum of P [105], but at higher biochar amendment rates the sorption maximum is higher than the unamended soil [29]. From these observations, it appears that the amendment rate of the biochar in this study was not sufficient to let the soil-biochar mixture to adsorb P more than the control. It was observed that, when the biochar rate increases, the pH of the soil-biochar mixture rises (Table 13), which affects the adsorption of P [351] due to the formation of more negative charges on the surface of the soil-biochar samples as confirm by the point of zero charge analysis, thus increasing repulsion of anionic P forms [32,352]. It is observed that, soil amended with biochar produced at higher temperature had a lower P sorption maximum for all four biochars. The electrical conductivity of amended soil was found to increase with biochar produced at higher temperature (Table 13) which will increase the ionic strength of solution and may reduce the positive electric potential of soil surface through a screening effect and ultimately reduced the P sorption [32]. At amendment rate of 20, 40 and 80 g/kg after 7 days of incubation, Q_{max} for SCH350 were 2266.50, 2047.84 and 1822.81 mg/kg which increased to 2406.70, 2112.20 and 1989.76 mg/kg after 60 days of incubation. This tendency was observed for all four biochar with respect to rise in incubation days. In general, it was observed that soil-biochar with cocoa pod husk biochar had a lower P sorption maximum as compare to those incubated with coffee husk biochar for 7 days of incubation, whereas, at 60 days of incubation the adsorption maximum were more or less the same. Other studies, however, showed reduction in phosphate sorption in acidic soils as a result of biochar application due to precipitation of Al^{3+} and Fe^{3+} (sites for phosphate complexation) [31] and increase in repulsion by the negative charges newly created in the soil, due to the presence of $-O^-$ and $–COO^-$ from biochar [33]. This is confirmed with the rise in soil organic carbon content (Table 13). In this study, we observe that biochar amended on soils serves as a source of P than as a sink, resulting in higher availability of P to soils with increasing biochar rate.

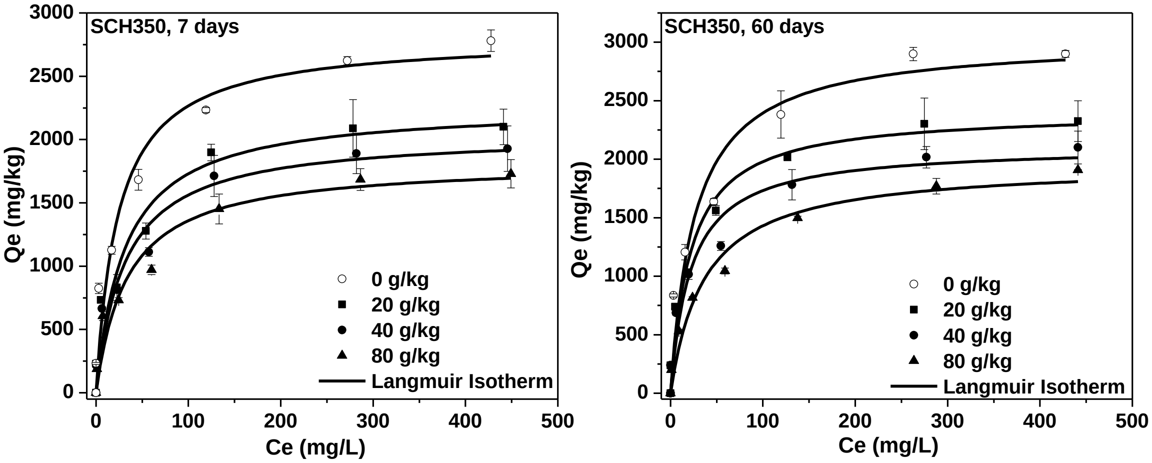


Figure 29: Langmuir phosphorus sorption isotherms for SCH350 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 day

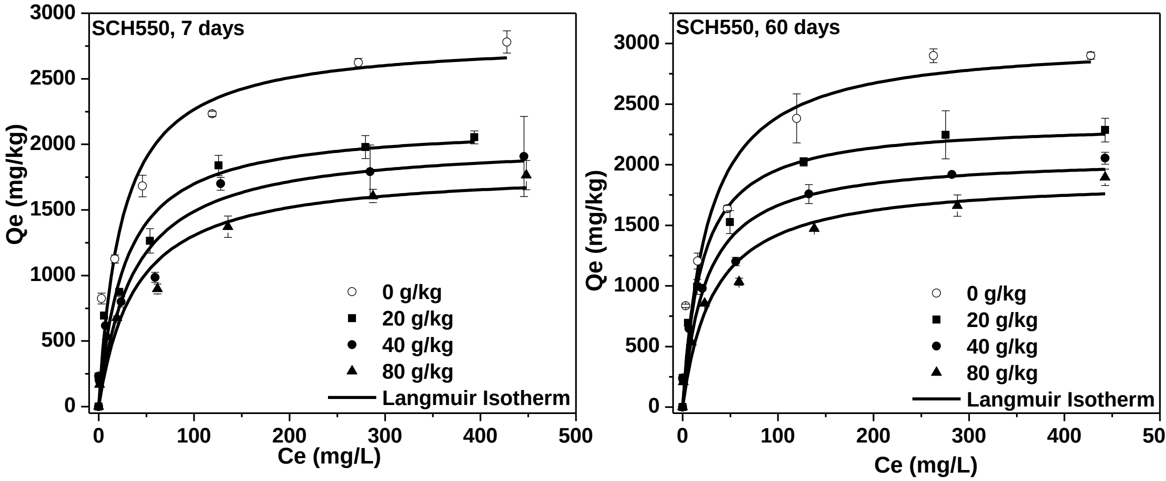


Figure 30: Langmuir phosphorus sorption isotherms for SCH550 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

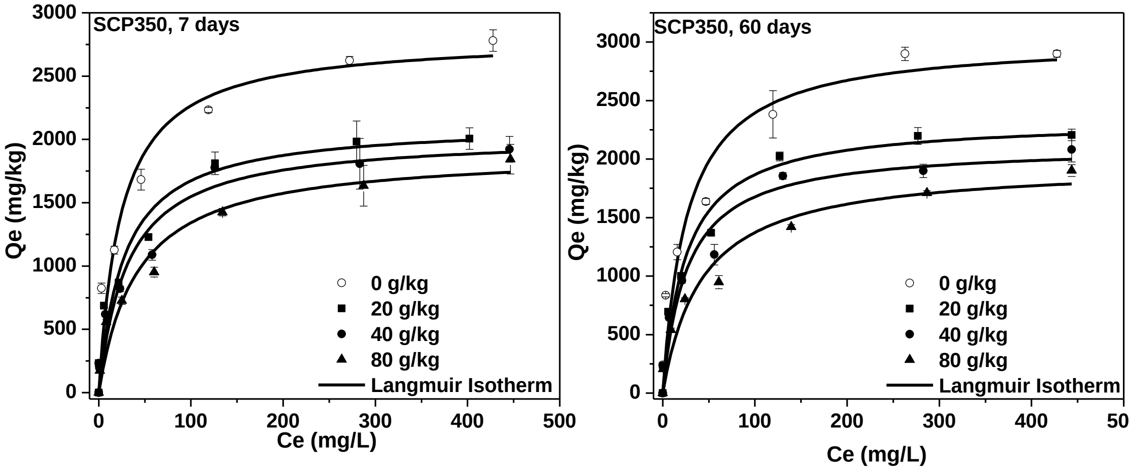


Figure 31: Langmuir phosphorus sorption isotherms for SCP350 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

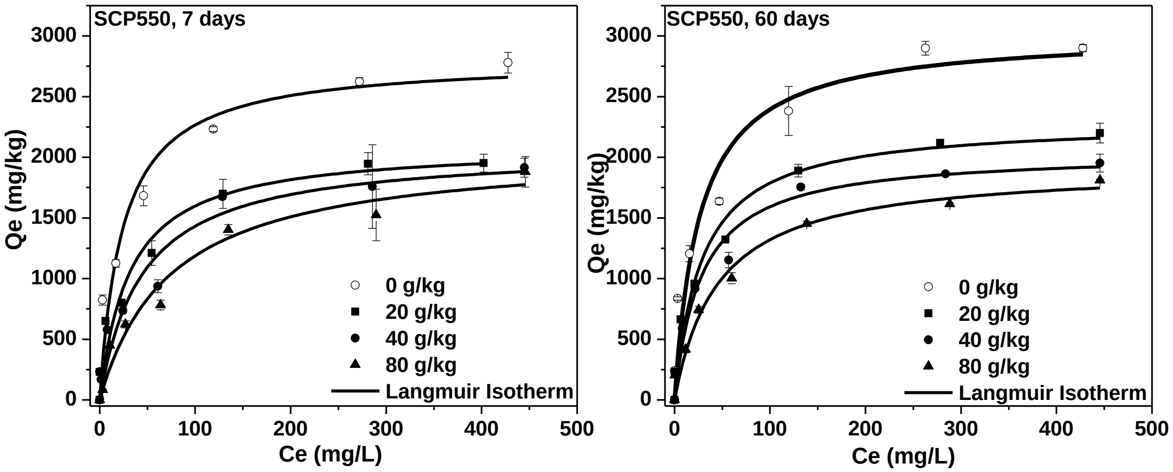


Figure 32: Langmuir phosphorus sorption isotherms for SCP550 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

Binding energy data (Table 15) obtained from Langmuir isotherm decline, with increasing amendment rate irrespective of biochar type and number of incubation days. For example, soil amended with CH550 for 60 days of incubation had a drop in binding energy from 0.0497, 0.0410 and 0.0303 L/kg and for SCP550 after 7 days of incubation; the drop was from 0.0318 to 0.0225 then 0.0134 L/kg for amendment rate of 20, 40 and 80 g/kg respectively. Also, the binding energy increase in the soil-biochar mixture amended with biochar produced at lower temperature i.e. in the order SCH350 > SCH550 and for SCP350 > SCP550. Also, binding energy increased with rising number of incubation days for each biochar type and corresponding amendment rate. For example the rise in binding energy from 7 to 60 days for soil-biochar mixture amended with 20 g/kg of CH550, was 0.0369 to 0.0497 L/kg, 0.0278 to 0.0410 for 40 L/kg and then from 0.0256 to 0.0303 L/kg for 80 g/kg and the case of SCP550 the binding energy was 0.0318 to 0.0352 L/kg, 0.0225 to 0.0353 for 40 g/kg and then from 0.0134 to 0.0217 L/kg for 80 g/kg. The order of decreasing binding energy of soil-biochar samples suggests that P can be easily desorbed. These results suggest that, compared to active sites in the original acidic soil, newly developed hydr(oxide) in the biochar-amended soil might retain phosphate ions more loosely [29,353]. Increase amendment rate in soil-biochar mixture results in a rise in pH, lower concentrations of free Fe, Al and Mn oxides which may be transform to Fe, Al and Mn hydroxides and reduced the availability of high energy sorption sites [354]. Generally, phosphates are strongly fixed to acidic soils not only through chemisorption on high-energy surfaces of Fe and Al oxides and hydroxides but also via precipitation of Al and Fe phosphate. However free Al and Fe concentrations in biochar-amended soil are lowered (Table 13) thereby reducing the availability of high energy sorption sites for phosphate ions [128].

In general, it was observed that soil-biochar mixture with cocoa pod husk had a lower P sorption maximum as compare to those incubated with coffee husk after 7 days of incubation, whereas, at 60 days of incubation the adsorption maximum were more or less the same. For all biochar, the P sorption maximum obtain from Langmuir isotherm model were greater than from experimental data indicating that all the biochar sites were not occupied by P.

Table 15: Langmuir parameters for soil-biochar incubated for 7 and 60 days

		7 days			60 days		
Materials	***Amendments***	K_L (Lkg^{-1})	Q_{max} (mg/kg)	R^2	K_L (Lkg^{-1})	Q_{max} (mg/kg)	R^2
SCH350	**20**	0.0321	2266.50	0.900	0.0462	2406.70	0.953
	40	0.0321	2047.84	0.914	0.0456	2112.20	0.930
	80	0.2932	1822.81	0.920	0.0259	1989.76	0.960
SCH550	**20**	0.0369	2158.46	0.924	0.0497	2354.38	0.968
	40	0.0278	2024.98	0.911	0.0410	2070.32	0.938
	80	0.0256	1815.06	0.936	0.0303	1891.18	0.945
SCP350	**20**	0.0367	2128.84	0.919	0.0398	2336.48	0.947
	40	0.0320	2031.83	0.932	0.0382	2116.30	0.933
	80	0.0239	1903.78	0.937	0.0233	1960.86	0.927
SCP550	**20**	0.0318	2100.26	0.927	0.0352	2295.46	0.952
	40	0.0225	2069.86	0.927	0.0353	2043.31	0.954
	80	0.0134	2069.43	0.952	0.0217	1927.41	0.974

Freundlich Isotherm Model

Figure 33, 34, 35 and 36 represents simulated Freundlich curves for the adsorption of P onto soil amended with biochar produced from coffee husk and cocoa pod husk at 350 °C and 550 °C incubated for 7 and 60 days at room temperature. This simulated curve profile, is similar to the Freundlich curve for S0. From Table 16, it is observed that the sorption capacities (K_F) of soil-biochar mixtures are less than the control (S0), which can be related to the lower P sorption maximum for soil-biochar mixture. Also, a decline in sorption capacity with increasing incubation rate for all the biochar type irrespective of incubation period was observed. An example of illustration, at 60 days of incubation, soil amended with CH350 showed a decrease in sorption capacity from 535.34, 459.87 to 287.53 mg/kg and with CP350 amendment, the decrease was from 483.25, 417.63 to 273.90 mg/kg with increase in amendment rate 20, 40 and 80 g/kg respectively.

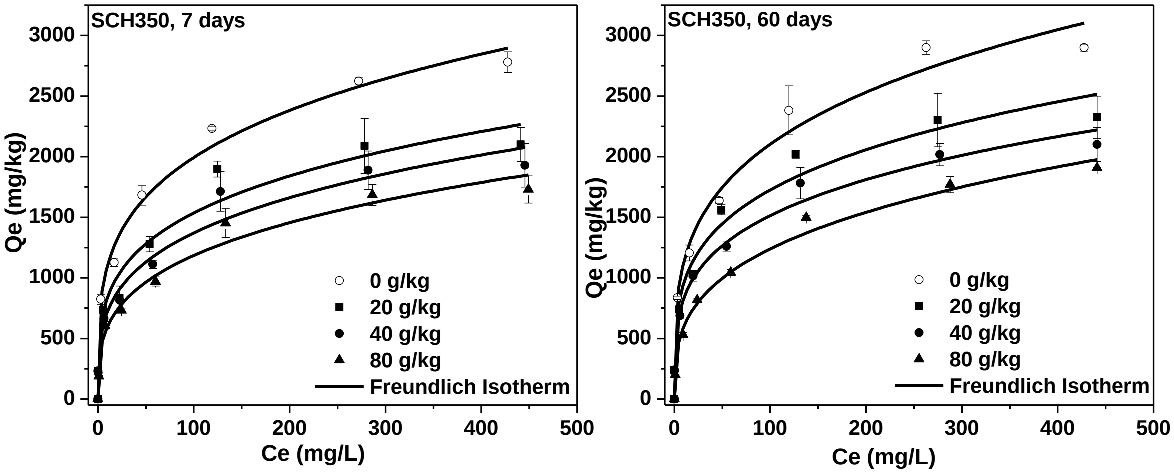


Figure 33: Freundlich phosphorus sorption isotherms for SCH350 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

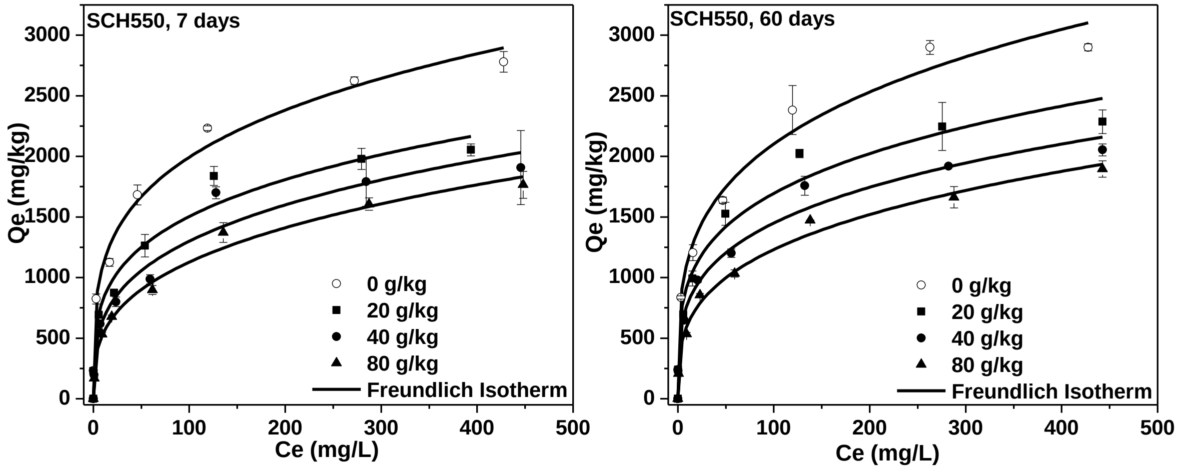


Figure 34: Freundlich phosphorus sorption isotherms for SCH550 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

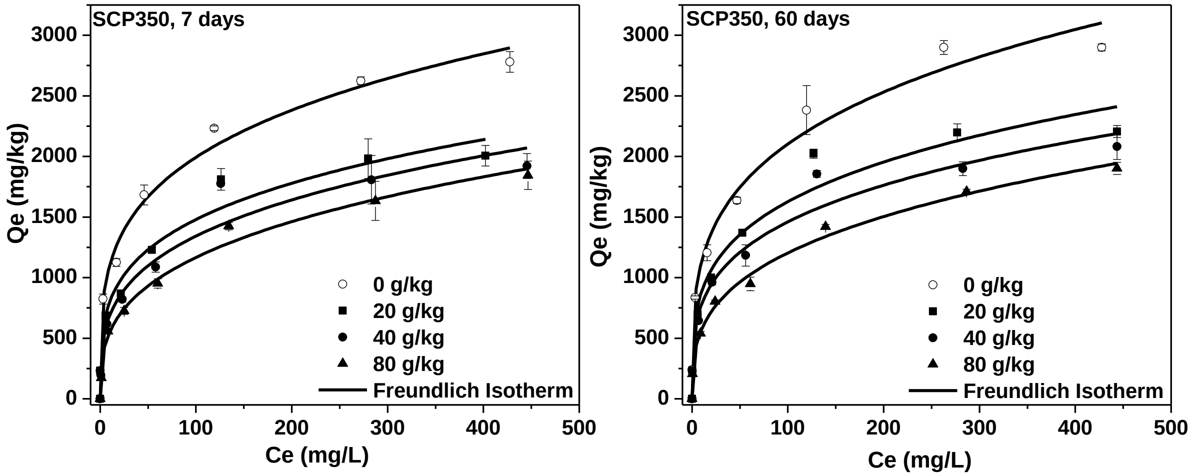


Figure 35: Freundlich phosphorus sorption isotherms for SCP350 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

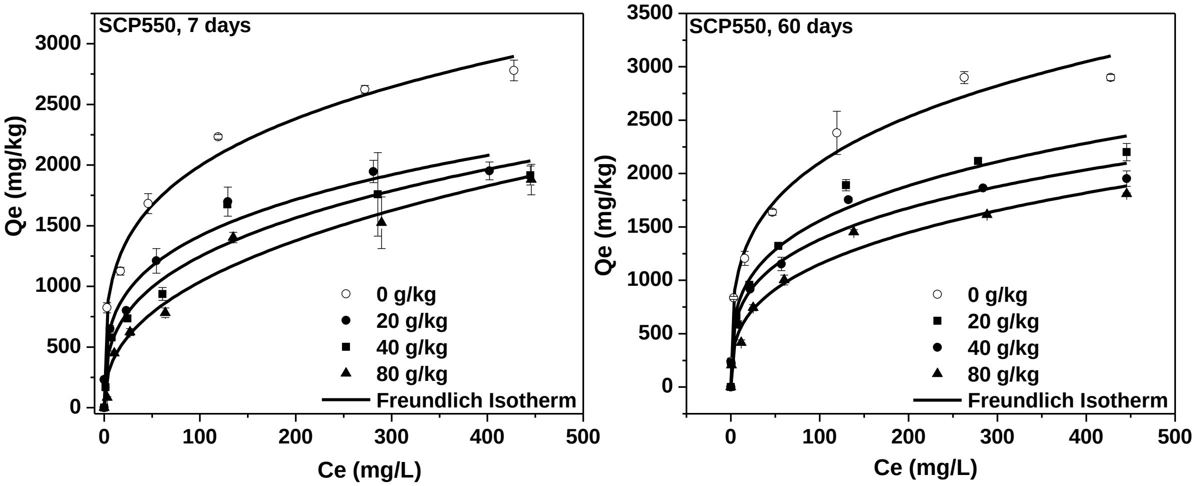


Figure 36: Freundlich phosphorus sorption isotherms for SCP550 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days

Soil amended with biochar pyrolysed at higher temperature, had a significant decrease in P sorption capacity. Moreover it was depicted that increase in incubation days from 7 to 60 days increase P sorption capacity of the soil-biochar samples for all biochar type. For example, comparing the rise in sorption capacity between 7 days and 60 days of incubation for SCH350 was 459.26 to 535.34 for 20 g/kg, 381.56 to 459.87 for 40 g/kg and 302.35 to 287.53 g/kg. The sorption intensity $\frac{1}{\mathrm{n}}$ is used to describe the heterogeneity of the adsorption surface. The affinity of P adsorption on soil-biochar, increases as $\frac{1}{\mathrm{n}} \approx 1$.

From Table 16, the sorption intensity of SCH350, SCH550, SCP350 and SCP550 is slightly greater than for S0 after 7 days of incubation. For 60 days of incubation, the sorption intensity of SCH350, SCH550, SCP350 and SCP550 at rate of 20 and 40 g/kg presents a relatively lower or the same sorption intensity with S0. Rather, with amendment rate of 80 g/kg, the sorption intensity was greater meanwhile for CP350 and CP550 soil amendment, the sorption intensity were higher than for S0 for all amendment rate. Increase in the number of incubation days; decreases the sorption intensity of P onto the soil-biochar mixture. Thus for greater $\frac{1}{n}$ values, the adsorption of phosphate to soil-biochar mixture was favourable and happened on heterogeneous surfaces.

Table 16: Freundlich parameters for soil-biochar samples incubated for 7 and 60 days

		7 days			**60 days**		
Material	**Amendment rate**	$\frac{1}{n}$	K_F **(mg/kg)**	**R²**	$\frac{1}{n}$	K_F **(mg/kg)**	**R²**
SCH350	**20**	0.2624	459.26	0.945	0.2541	535.34	0.965
	40	0.2777	381.56	0.952	0.2587	459.87	0.979
	80	0.2966	302.35	0.961	0.3181	287.53	0.984
SCH550	**20**	0.2659	442.10	0.966	0.2554	522.89	0.961
	40	0.2987	328.55	0.938	0.2680	421.94	0.974
	80	0.3236	254.09	0.981	0.3039	303.71	0.984
SCP350	**20**	0.2659	434.68	0.966	0.2640	483.25	0.951
	40	0.2897	353.65	0.927	0.2718	417.63	0.955
	80	0.3255	260.56	0.979	0.3215	273.90	0.991
SCP550	**20**	0.2775	394.31	0.969	0.2764	436.19	0.970
	40	0.3287	274.20	0.931	0.2793	381.66	0.952
	80	0.4089	157.72	0.954	0.3301	251.66	0.969

Previous studies were consistent with this observation as reported by Yao and co-workers in 2011 [323], who indicated a low adsorption capacity with biochar derived from sugar beet tailing same as Xu and co-workers in 2014 [29] incubated acidic soil samples with wheat straw biochar. The decrease in sorption capacity of the soil-biochar mixture which is closely related with sorption maximum from Langmuir data can be due to variation in physicochemical properties of the samples. Increase in pH and PZC of the samples, will lead to increase in negative charge surfaces, thereby increasing repulsion thus decline in P sorption capacity [352]. Higher pH depresses the formation of HPO_4^{2-}, which is preferentially adsorbed by soil colloids [29].

3.3.4 Phosphorus desorption from soil and soil biochar mixture

The extent of desorption of P from these samples can indicate the degree of P availability in the soil solution and to plants. In this work, P desorption percentage was used to evaluate the quantity of P desorbed from soil and soil-biochar mixtures as presented in Table 17. Results showed that, the amount and percentage of P desorbed were influenced by biochar type, the rate of amendment and the number of incubation days. P desorption from biochar amended soils were greater than unamended soil. This is due to the fact that during amendments of soil with biochar, P is released from biochar and sorb onto strong adsorption sites which is not reversible [350]. This process leaves fewer adsorption sites for P, therefore newly sorbed P will have low energy adsorption sites, which may results to ease in desorption. Also, the presence of acid-functional groups such as carboxylic and phenolic groups on the biochar causes P removal from clay minerals through ligand exchange and or enhanced ligand dissociation of oxides and hydroxides of Fe and Al [355]. Cocoa pods biochar amended soil have a greater P desorption percentage than coffee husk biochar amended soil samples. Soil-biochar mixtures with high temperature pyrolysis biochar desorbed P higher than at low pyrolysis temperature biochar at amendment rate of 40 g/kg and 80 g/kg. Whereas at 20 g/kg, there was no significant change in P desorption. It was observed that at higher pyrolysis temperature biochar adsorb less than low pyrolysis temperature biochar for the same amendment rate, but desorbs more. Increase in amendment rate, elevate the desorption percentage of P from the soil-biochar mixtures. The desorption percentage was more than about 10 % rise for all biochar type from 20 mg/kg to 80 mg/kg amendment rate. Increase in incubation days for soil-biochar mixtures resulted in a decline in desorption percentage of P. In all cases, increasing P desorption percentage, is related to a decline in binding energy for soil-biochar samples as can be seen in Table 16. Previous research corroborated the assertion that decrease in binding energy result to ease in desorption of P which was attributed to increase in soil pH with biochar application [105].

Table 17: Percentage desorption of P from soil and soil-biochar mixture

		7 days			60 days		
Material	**Amendment Rate**	**P_{sorbed}**	**$P_{desorbed}$**	**DP (%)**	**P_{sorbed}**	**$P_{desorbed}$**	**DP (%)**
S0	**0**	1571.19	429.00	27.30	1516.16	412.45	27.20
SCH350	**20**	1223.21	384.62	31.44	1299.33	376.69	29.00
	40	1164.72	392.05	33.66	1113.33	368.32	32.63
	80	1017.58	412.37	40.52	894.49	346.67	38.76
SCH550	**20**	1213.08	452.01	37.26	1216.33	375.85	30.90
	40	1146.62	389.28	33.95	1076.17	360.69	33.52
	80	846.79	394.52	46.59	944.18	372.41	39.44
SCP350	**20**	1205.46	392.95	32.60	1186.92	373.25	31.45
	40	1137.60	375.57	33.01	1058.28	366.95	34.67
	80	882.53	386.37	43.78	890.86	361.73	40.60
SCP550	**20**	1161.99	381.29	32.81	1205.12	365.76	30.35
	40	1052.36	360.35	34.24	1013.20	385.49	38.05
	80	858.76	364.95	42.50	820.84	332.06	40.45

3.4 Partial conclusion

Soil amended with biochar change the fixation and release ability of P as compared to unamended soil. P sorption capacity of amended soil reduced with increase amendment rate and elevated pyrolysis temperature. Soil amended with biochar from CP had a lower P sorptiom maximum as compare to CH. From the Langmuir model, P sorption maximum were greater than from experimental data, indicating not all sorption sites were occupied. The sorption intensity of amended soils after 7 days of incubation was greater than the control. Increase in the number of incubation days; decreases the sorption intensity of P onto the soil-biochar mixture. On the other hand, the desorption process of P from soil-biochar mixture was enhance at higher biochar rate and higher temperature. From this study we can suggest that P retention and availability can be modulated when biochar are applied at a convenient rate and pyrolysed at an appropriate temperature of about 550 °C. Thus, biochar can be appropriate for P management practices since it alleviate acid soils, decrease P retention from the soil solution phase and ease P release from the solid phase to the soil solution thereby improving the conditions for plant growth as compared to acid soils. Field study should be done with the application of biochar to evaluate the fate of applied phosphate fertilizers in acidic soils.

GENERAL CONCLUSION AND PERSPECTIVES

This chapter provides (i) a general run through of the main achievements of this study and (ii) some research perspectives.

General conclusion

Worthy of the increasing interest in biochar as a soil amendment to overcome some soil limitations, the aims of this study were to produce biochar from abundant and cheap biomass and amend acid soil to study the effect on the soil chemical properties and the effect of P sorption and desorption on the amended acid soil.

This research revealed that the characteristics of biochar produced were a function of the pyrolysis temperature and biomass type. Biochar produced from cocoa pod husk had a higher liming potential as compared to coffee husk, and increasing the temperature of pyrolysis resulted in the same trend. That is, CP550 had higher $CaCO_{3(eq)}$, alkalinity, and acid-neutralizing capacity compared to CH550. All four biochars presented complex functional groups such as O- and –COO- as revealed by the Infrared spectra, with their band intensities decreasing with rising temperature. Minerals shown by the x-ray pattern presented sharp bands of calcite, sylvite, and quartz as the main minerals in the biochar. The presence of these minerals contributed to the alkaline nature of the biochar. Images obtained from SEM analysis presented a rough surface with pores; this contributed to the water holding capacity of the soil and could increase the soil porosity. The nutrient content of the biochar was evaluated as the availability of P. Phosphorus was released from the biochar and was higher in cocoa pod husk biochar than in coffee husk biochar, irrespective of the temperature. Thus, biochar can be a source of P in soil.

The main findings of the effect of biochar amendment rate and incubation time on soil chemical properties are summarized as follows:

- An increase in biochar rate yielded an increase in soil pH as compared to the control, and the pH of soil increases with incubation time. CP550 caused the greatest increase in soil pH.
- The soil EC increased with an increase in biochar rate and incubation time. Biochar produced at 550 ºC resulted to higher increase compared to those produced at 350 ºC.
- The fertility aspect of the biochar was demonstrated by the increase in available P upon the addition of biochar. Available P increased with biochar rate and incubation time. It was observed that the readsorption of P at higher dosages increased with increasing incubation time.

- A drastic drop in the quantity of soil acidity, exchangeable Al, and Fe was observed with an increase in biochar rate and incubation time.
- An increase in SOC with biochar rate. An increase and then a decrease in SOC were more pronounced with biochar produced at 350 ºC as compared to biochar produced at 550 ºC.

The result of the investigation of P sorption and desorption on biochar amended soils reveal a general decline in P sorption capacity. The decrease was predominant with rising biochar and increasing temperature. The decrease in sorption capacity of the soil-biochar mixture, which is closely related to the sorption maximum from Langmuir data, can be due to variations in the physicochemical properties of the samples. An increase in pH and PZC of the samples leads to an increase in negative charge surfaces, thereby increasing repulsion and a decline in P sorption capacity. In general, it was observed that the soil-biochar mixture with cocoa pod husk had a lower P sorption maximum as compared to those incubated with coffee husk after 7 days of incubation, whereas at 60 days of incubation, the adsorption maximum was more or less the same. For all biochar, the P sorption maximums obtained from the Langmuir isotherm model were greater than those from experimental data, indicating that all the biochar sites were not occupied by P. The desorption process of P from the soil-biochar mixture was enhanced at higher biochar rate and higher pyrolysis temperature. The desorption percentage rose by more than 10 % rise for all biochar types from 20 mg/kg to 80 mg/kg. An increase in incubation days for soil-biochar mixtures resulted in a decline in desorption percentage of P. In all cases, increasing P desorption percentage is related to a decline in binding energy for soil-biochar samples.

The effect of biochar on these soil chemical properties was mainly due to the intrinsic chemical properties of the biochar. Thus, clear knowledge of the liming and fertilizing properties of biochar and its effect on soil properties is useful. Moreover, biochar can be appropriate for P management practices since it alleviates acid soils, decreases P retention in the soil solution phase, and eases P release from the solid phase into the soil solution, thereby improving the conditions for plant growth as compared to acid soils. This research highlights the fact that biochar usage results in a multiple "win" strategy in that it is a source of lime and, at the same time, a source of P fertilizer nutrients.

Perspectives for future study

Based on the results obtained from this research work, the following perspectives were made:

- A detailed analysis of the produced biochar needs to be done, such as CEC, total N, total C, specific surface area to enhance the elucidation of the mechanisms of soil acidity improvement and P adsorption.
- The Hedley fractionation method for assessing P fractions should be included to further understand P fractions in the soil-biochar mixture.
- This study could be redone on a large scale by using different initial biomasses to produce biochar and amendments done on different soil type, to select and match a biochar type to the soil type.
- A field or greenhouse experiment could be conducted using a test crop (e.g., maixe, common beans) under the same experimental conditions as those used in this study.
- Also, biodiversity studies should be carried out in order to assesss the impact of biochar on microbial or pathogenic microbial soil communities.

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ANNEXE

1. Publications

i. **POUANGAM NGALANI G**, DZEMZE KAGHO F, NANSEU NJIKI CP, PRUDENT P, ONDO JA, NGAMENI E. 2022. Effects of coffee husk and cocoa pods biochar on the chemical properties of an acid soil from West Cameroon. *Archives of Agronomy and Soil Sciences*, 69(5), 744-758. doi:10.1080/03650340.2022.2033733.

ii. **POUANGAM NGALANI** G, ONDO JA, NJIMOU JR, NANSEU NJIKI CP, PRUDENT P, NGAMENI E. 2023. Effect of coffee husk and cocoa pods biochar on phosphorus fixation and release processes in acid soils from West Cameroon. *Soil Use and Mangement*, 00, 1-16. doi:10.1111/sum.12894.

2. Abstracts, posters and presentations in conferences

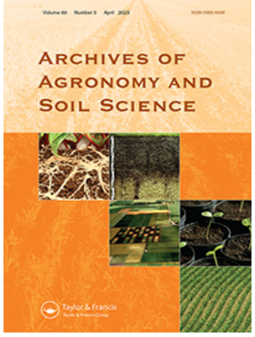
i. **POUANGAM NGALANI Gilles**, ONDO Jean Aubin, NGAMENI Emmanuel, Lime effect on soil acidity: exchangeable Al, Fe, Ca, Mg and electrical conductivity in tropical acid soils (case of Nkolbisson), Journées de Chimie Analytique, 8éme édition, Douala, Cameroon, 30 Septembre, 1 – 2 Octobre 2015. (*Poster presentation*)

ii. **POUANGAM NGALANI Gilles**, ONDO Jean Aubin, NGAMENI Emmanuel, Suivi de la dynamique des polluants dans les ecosystemes, Journées de Chimie Analytique, 9éme édition, NGaoundéré, Cameroun, 27 – 29 Septembre 2017. (*Poster presentation*)

iii. **POUANGAM NGALANI Gilles**, DZEMZE KAGHO Frank, PRUDENT Pascale, ONDO Jean Aubin, NGAMENI Emmanuel, Potential P and lime in coffee husk and cocoa pods husk derived biochar with aim of agronomic benefits, Journées de Chimie Analytique, 10éme édition, Yaounde, Cameroon, 4 – 6 Septembre 2019 (*Poster and Oral presentation*)

3. Prices

1. **Best Oral presentation JCA2022** in the thematic « Biotechnologie environnemental et valorisation des bioressources ». Journees de Chimie Analytique, 11th Edition, Yaounde, 24 – 26 August 2022.
2. **Best Poster Presentation Doctoriales_URFD_Chimie et Application,** University of yaounde 1, 20 – 21 October 2022.



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RESEARCH ARTICLE

Effects of coffee husk and cocoa pods biochar on the chemical properties of an acid soil from West Cameroon

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ABSTRACT

Evaluation of liming and fertility properties of biochar on acid soil was studied in this work. Selected soil properties such as pH, electrical conductivity (EC), exchangeable acidity (Ex Ac), exchangeable Al (Ex Al), exchangeable Fe (Ex Fe), available P and, soil organic carbon (SOC) were examined under the effect of biochar amendments. The acid soil was treated with biochar issued from coffee husk (CH) and cocoa pods (CP) pyrolyzed at 350°C and 550°C for 4 hours at amendment rate of 0, 20, 40 and 80 g kg^{-1} and an incubation time of 7, 14, 30, 40 and 60 d. Biochar amendments significantly increased soil pH, soil EC with respect to control and decrease in exchangeable acidity was observed. Results show that biochar improved available P in acid soil, though re-adsorption occurred with increasing incubation time. A significant increase in SOC is observed as compared to control. The impact of biochar on these acid soil chemical properties is due to the properties which are dependent on the biochar type and pyrolysis temperature. Thus, biochar can play the dual role of a liming agent and a source of P fertilizer nutrients.

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Introduction

Soils in Central Africa and especially in Cameroon are acidic (Takow et al. 1991; Takoutsing et al. 2016) and are manifested with dominance in hydrogen (H^+) and Aluminium (Al^{3+}) ions in the soil solution (Ondo 2011). The presence of soluble Al causes toxicity which inhibits both cell elongations, cell division and also interferes with the uptake, transport and use of several essential elements (Kochian et al. 2005) resulting in a great reduction in crop yield. Phosphorus in the form of phosphate availability in acid soils is extremely low due to the large amounts of Al and Iron (Fe) oxides which retain phosphorus (P) (Balemi and Negisho 2012). Coupled with the acidity of soils in the tropics, sustainable agriculture faces the constraint of low soil organic matter content due to accelerated mineralization (Tiessen et al. 1994), erosion, leaching (Roose and Barthes 2001) and also inappropriate cultivation practices.

To remediate these multiple limitations, amendments are the best ways to: (1) alleviate soil acidity by using lime (Pagani and Mallarino 2012), composted waste (Haynes and Mokolobate 2001), and wood ash (Nkana et al. 2002). The rise of soil pH and alleviation of Al^{3+} from solution are mainly due to (a) the consumption of H^+ and precipitation of soluble and exchangeable Al and Fe by OH^- (Fageria et al. 2014), (b) flow of protons from the soil to the organic matter sites and complexation of Al by soluble humic materials, by soluble organic acids, and by newly-formed organic matter (Haynes

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and Mokolobate 2001); (2) improvement of available P by (a) direct P fertilizer (Ondo et al. 2017), application of rock phosphate (Basak and Biswas 2016), which is due to the saturation of the adsorption sites of P on Al and Fe oxides (Fischer et al. 2018); (3) organic carbon can be added in soil using organic waste such as crop residues, animal manures, municipal solid waste, bio-solids, etc. (Park et al. 2011).

The above approach has its limitations such as economical, over liming which may precipitate phosphate with Ca, excess use of P fertilizer which may lead to eutrophication and direct application of manure which may pose a risk of surface – and groundwater impairment (Parvage et al. 2013). Also, the poor stability of organic matter due to much labile C in crop residue or compost (Tiessen et al. 1994). An alternative to these different limitations is the use of biochar which gives the possibility to solve several problems at the same time creating a lot of hopes.

Biochar is a product derived from the pyrolysis of biomass in an atmosphere containing little or no oxygen (Joseph and Lehmann 2009). One of the major reasons in which biochar is applied is its effect on soil quality and plant growth (Wu et al. 2019). Generally, biochar has a higher pH, higher CEC, higher porosity than the uncharred organic amendments (Joseph and Lehmann 2009). Many researchers have shown that biochar itself is a potential source of P (Angst and Sohi 2013; Manolikaki et al. 2016). Also, biochar consists of condensed aromatic forms of organic carbon which are recalcitrant and do not decompose easily in soil (Atkinson et al. 2010), preventing carbon from returning to the atmosphere as carbon dioxide (CO_2) within a short period.

Biochar prepared from different feedstock under a range of pyrolysis conditions exhibits major differences in their physical, chemical, and adsorption properties (Rehrah et al. 2014). The study of changes in soil chemical properties due to the application of biochar is still current research in view to better understand the mechanisms sustaining these changes. The hypothesis for this research is based on the fact that, biochar obtained from different feedstock and produced at different temperatures will have an effect on soil physicochemical properties. The objective of this study is to evaluate the effects of biochar rate and incubation time on soil chemical properties (soil pH, electrical conductivity, soil acidity, exchangeable Al, available P and soil organic carbon).

Materials and methods

Soil sampling and feedstock collection

Topsoil samples (ten) were collected randomly (depth of 0–15 cm) on a 2-hectare mixed cocoa and coffee farm in Bafang, in the Upper-Nkam Division the West region of Cameroon. The soil samples were air-dried, crushed, sieved through a 2 mm sieve and stored in plastic bags for physicochemical analyses and incubation studies. Coffee husks and cocoa pods were collected from coffee processing factories and cocoa farms respectively, located in Bafang. These feedstocks were dried and grind to pass through a 2 mm sieve to ensure uniformity of samples during pyrolysis and then dried at 105°C.

Biochar preparation

Feedstocks were placed in a covered ceramic crucible and put in a muffle furnace. The pyrolysis processes were done at two different temperatures (350 °C and 550 °C) at pyrolysis rate of 10 °C min^{-1} and held constant for 4 h. After the 4 h duration, the biochar samples were left to cool in the muffle furnace to room temperature, and then it was grinded to very fine particles (< 2 mm sized fraction). The biochars were labelled as CH350 and CP350, CH550 and CP550 for coffee husk and cocoa pods produced at 350 °C and 550 °C respectively. Biochar samples were kept in polythene bags in a warm environment for characterization and incubation studies.

Laboratory incubation design for soil-biochar

To examine the effects of biochar on cited parameters in the objectives, incubation experiment was established in the laboratory. 100 g of dry soil was mixed with biochar at application doses of 0, 20, 40 and 80 g kg^{-1} in transparent plastic pots and mixed thoroughly. Then, the potted samples were wetted with deionized water to 70% of field water holding capacity of the soil and left for 7, 14, 30, 45 and 60 d of incubation with lids having small holes on them to prevent the rapid evaporation of soil moisture and permit the passage of air. All treatments were done in quadruples and left at room temperature. Every three days, water was added to maintain constant moisture content throughout the experiment. At the end of incubation periods, the samples were ground and sieve to < 2 mm and then store back in their incubation plastic cups.

Analyses of biochar, soil and soil-biochar mixture

Biochar, soil and soil-mixture analysis

Biochar ash content was determined by calculating the percentage of remaining solid ash to biochar mass after dry combustion of biochar samples in a muffle furnace at 750 °C for 6 h (Rehrah et al. 2014). Construction of the acid-base titration curve to evaluate biochar alkalinity was determined by the acid-base titration method (Yuan et al. 2011). The acid-neutralizing capacity of biochar was determined by mixing biochar in a solution of HCl and back titrating with NaOH (Martinsen et al. 2015). $CaCO_3$ equivalence from biochar samples was determine by the method proposed by Rayment and Lyons (2011). Fourier transform infrared spectroscopy (FTIR) was recorded on an Alpha spectrometer from Bruker Optics. The scans were obtained in the range from 400 to 4000 cm^{-1}. The XRD patterns of the prepared biochars were registered with CuKα radiation between 5 and 80° (2θ) for 7 h in steps of 0.03° using Bruker D4. Biochar pH and EC were determined were measured using 1:5 solid: solution ratio after shaking for 30 min in deionised water (Singh et al. 2010) while soil and soil-biochar mixture pH and EC were determined by shaking water and deionised water in the ratio 1:2.5 and 1:5 respectively (Pansu and Gautheyrou 2007). Available P from biochar, soil and soil-biochar was determined using the Olsen P solution (0.5 M $NaHCO_3$ at pH 8.5) and the aliquot taken for P spectrocolorimetry determination (Olsen et al. 1954; Murphy and Riley 1962). Quantification of organic carbon from biochar, soil and soil-biochar mixture was determined by the Walkley and Black method (Walkley and Black 1934). Exchangeable acidity, exchangeable Al (Ex Al) and exchangeable Fe (Ex Fe) were based on the principle of sample washing with a saline solution of 1 M KCl solution (Pansu and Gautheyrou 2007), then titrating an aliquot for exchangeable acidity and exchangeable Al determination. Ex Fe was determined by Fe-ortho-phenanthroline complexation and absorbance read with visible-spectroscopy.

Statistical analyses

Statistical analyses were done using Excel 2013 and graphics using Origin 6.0. A one-way analysis of variance was performed for each incubation time interval, amendment rate, biochar type and a Two-way analysis of variance was performed by crossing the following dependent factors: incubation time interval, amendment rate and biochar type. The significant difference between the factors means for parameters under analysis were determined at a 5% level of significance ($\alpha = 0.05$). A Pearson correlation and t-test was performed to measure the strength of correlation and significance of the factors on the parameters under study.

Results and discussion

Biochar characterisation

From Table 1, biochar yield varied with biochar type and pyrolysis temperature. The biochar yield of CH and CP reduced significantly ($p < 0.05$) from 38.7% to 30.3% and 38.4% to 32.0% for pyrolysis temperature of 350 °C and 550 °C respectively. The decrease in yield is due to the volatilization of C, O and H compounds (Waqas et al. 2018). The percentage yield is interesting and can be economically feasible for small-scale farmers. All biochars were basic due to the presence of ash, alkali salts, carbonates and biocarbonates (XRD spectra, Figure 2). High pH values of CP and CH biochar have been reported in previous work (Martinsen et al. 2015; Domingues et al. 2017). Electrical conductivity significantly ($p < 0.05$) varied with biochar type and significantly ($p < 0.05$) increased with pyrolysis temperature (Table 1). Cocoa pods biochar had greater EC values as compared to CH biochar for the same pyrolysis temperature due to increasing amount of soluble salts in the ash thus biochar produced cocoa pods generally has higher EC values (Cantrell et al. 2012; Rehrah et al. 2014). Ash content varied with biochar type and pyrolysis temperature. From Table 1 CH and CP biochars, ash content increased significantly ($p < 0.05$) due to the condensation of mineral elements/compounds (Kloss et al. 2012; Waqas et al. 2018) which confirms with the increase in peaks of minerals observed on the XRD spectrum and the degradation of the organic part of the biomass as can be seen on the FTIR spectra. It was observed that liming potential increased significantly ($p < 0.05$) with pyrolysis temperature for both biochars with lime greater in CP than CH. Increasing liming potential is due to high level of carbonates and bicarbonates (XRD spectra; Figure 2). High liming value has previously been reported, indicating the presence of calcite and other carbonate minerals. The acid-neutralising capacity of CP biochar was significantly ($p < 0.05$) higher than those of CH biochar irrespective of pyrolysis temperature. This was attributed to an increase in alkaline component such as calcite, kalicinite (XRD spectrum; Figure 2) and the presence of $-O^-$ and/or $-COO^-$ groups which can fix H^+. So we can hypothesize a greater H^+ consumption by CP biochar in acid soils as compare to CH biochar for the same temperature of pyrolysis. Biochar produced in this study can be considered as a source of available P. It is higher in biochar produced from CP than those produced from CH. Results from past research have proven biochar as a source of P (Mukherjee and Zimmerman 2013; Manolikaki et al. 2016). From Table 1, the data obtained indicated that all four biochars were alkaline, with alkalinity varying with pyrolysis temperature and biomass type. Data gives the biochar alkalinity when titrated to pH 7.0 and 2.0 and calculated from Figure 1. Biochar produced from CP has alkalinity almost twice that of biochar produced from CH. The plateau region observed in Figure 1 for CH550 and CP550, suggests a relatively higher buffer capacity for acids in the pH range at which the titration curve plateau occurred (Yuan et al. 2011).

FTIR and XRD analyses

From FTIR in Figure 2, all four biochar presented a dome centered at 3418 cm^{-1}, which was attributed to the O–H stretching vibration of hydrogen-bonded hydroxyl groups from phenolic, carboxylic or alcohol hydroxyl group (Keiluweit et al. 2010). The peak at 2925 cm^{-1} and 2966 cm^{-1} on the spectrum of CH350 and CP350 respectively corresponded to the asymmetric C–H stretching vibration in aliphatic compounds suggesting the presence of cellulose and hemicellulose (Usman et al. 2015). The peaks appearing at wavenumber 1594 cm^{-1}, 1577 cm^{-1} very intense on CH350 and CP350 and 1559 cm^{-1}; 1576 cm^{-1} less pronounce on CH550 and CP550 corresponded to the C = C aromatic stretching and C = O stretching of conjugating ketones and quinones (Behazin et al. 2016). The absorption bands at 1410, 874, and 702 cm^{-1} for CH550 1406, 872, and 694.1 cm^{-1} for CP550 corresponded to the in-, out plane bending and asymmetric stretching vibrations respectively of C–O–C which indicate the presence of calcite and other mineral carbonates mineral in the biochar (Cao and Harris 2010). These peaks were not observed in CH350 and CP350 due to very low carbonate content as observed with the $CaCO_{3(eq)}$ equivalence (Table 1). The band around 1376 cm^{-1} and 618 cm^{-1} on CH350 and CP350 spectrum indicates the presence of O–H bending mode and the

Table 1. The yield and properties of biochar from coffee husk and cocoa pods produced at different temperatures.

									Alkalinity	
	Yield	Ash	pH	EC	$CaCO_{3eq}$	Acid-neutralizing capacity	Available P	Organic carbon	pH = 7	pH = 2
Biochars	(%)	(%)		(mS cm^{-1})	(%)	(cmol + kg^{-1})	(mg kg^{-1})	(g kg^{-1})	(cmol + kg^{-1})	
CH350	38.7 ± 0.7	16.7 ± 0.2	9.33 ± 0.01	9.66 ± 0.60	4.0 ± 0.0	151.9 ± 2.3	866.02 ± 2.4	67.10 ± 1.10	15.2	70.4
CH550	30.3 ± 0.7	24.1 ± 0.4	9.69 ± 0.01	20.65 ± 0.21	12.2 ± 0.1	252.5 ± 2.3	954.54 ± 23.18	6.67 ± 0.30	42.7	140.5
CP350	38.4 ± 0.6	21.9 ± 0.1	9.53 ± 0.02	18.06 ± 0.20	10.1 ± 0.0	198.1 ± 3.7	1232.45 ± 16.34	76.10 ± 1.40	22.7	120.3
CP550	32.0 ± 2.0	29.0 ± 0.3	9.63 ± 0.01	30.50 ± 0.28	14.2 ± 0.1	340.7 ± 5.4	1076.90 ± 42.25	11.01 ± 0.10	71.7	219.7

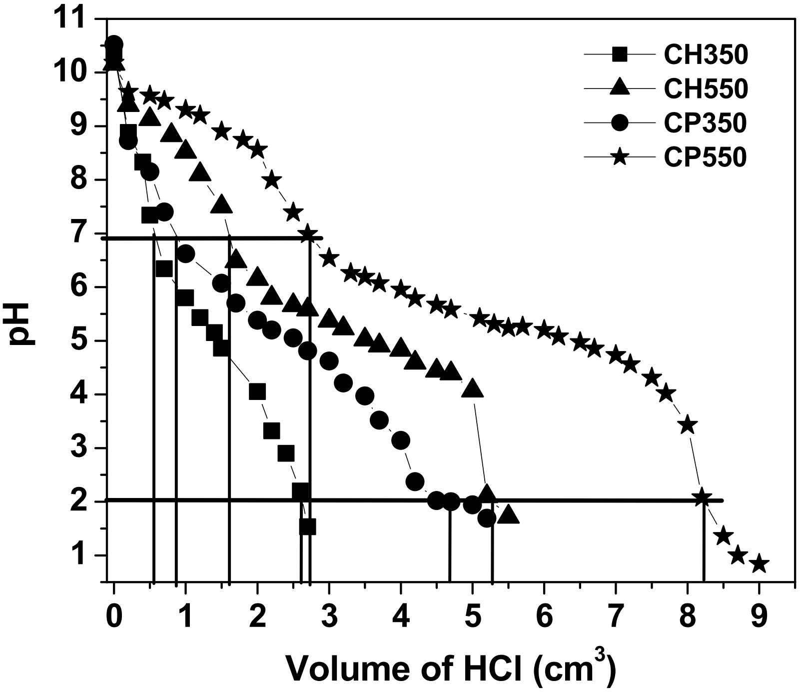

Figure 1. Acid-base titration curves of biochars produced from coffee husk and cocoa pods at different pyrolysis temperatures.

deformation out-of-plane of the C-O-H bond of phenol (Cantrell et al. 2012; Waqas et al. 2018). Additionally, with the presence of high level of quartz observed in the XRD spectra for CH550 and CP550, the bands at 1007 cm^{-1} and 832 cm^{-1} were attributed to silica (Keiluweit et al. 2010). Biochar production temperature affected the existing functional groups due to the dehydration of the ligneous and cellulosic contents and reduction in the aliphatic group with an increase in temperature of production. Furthermore, increase in temperature resulted in the presence of inorganic functional groups (carbonates) which is consistent with the increase in ash content and the presence of more crystalline minerals as seen on the XRD spectra.

The XRD spectra analysis depicts the structure and chemical composition of biochar. The biochar produced presented a variety of mineral crystals, with more in biochar produced at 550°C than those at 350°C. The XRD spectrum of all four biochar showed a broadband hump ($2\theta = 15–30°$) which confirms the presence of a largely poorly crystalline carbon-rich phase, due to increase in the aromatic carbon (Cao and Harris 2010; Singh et al. 2010). The intensity of the dome between $2\theta = 15–30°$ decreases with increase in temperature indicating the increase in the crystallinity of the carbon-rich phase. In Figure 3(c,d), peaks of quartz (Q) minerals in all four biochar, Calcite (C) and kalicinite in CH550, CP350 and CP550. The XRD spectrum for CH350 did not indicate any peaks for calcite and kalicinite minerals. Sylvite (S) minerals occurred at 2.22 Å for CP350, 3.15, 2.22 and 1.84 Å for CP550. From the spectra, peaks are sharp and intense at higher temperatures indicating the presence of more alkaline crystalline minerals. This observation was consistent with the acid-base titration curve for evaluation of biochar alkalinity (Figure 1) with a plateau for CH550 and CP550 due to buffering action of carbonates and also higher $CaCO_3$eq(%) (Table 1). Results obtained are consistent with the previous work done (Yuan et al. 2011; Domingues et al. 2017).

In conclusion, biochar characteristic depends on the feedstock type and pyrolysis temperature. We can hypothesize that amending acid soils with these biochars will have a distinctive effect on the chemical properties of the soil.

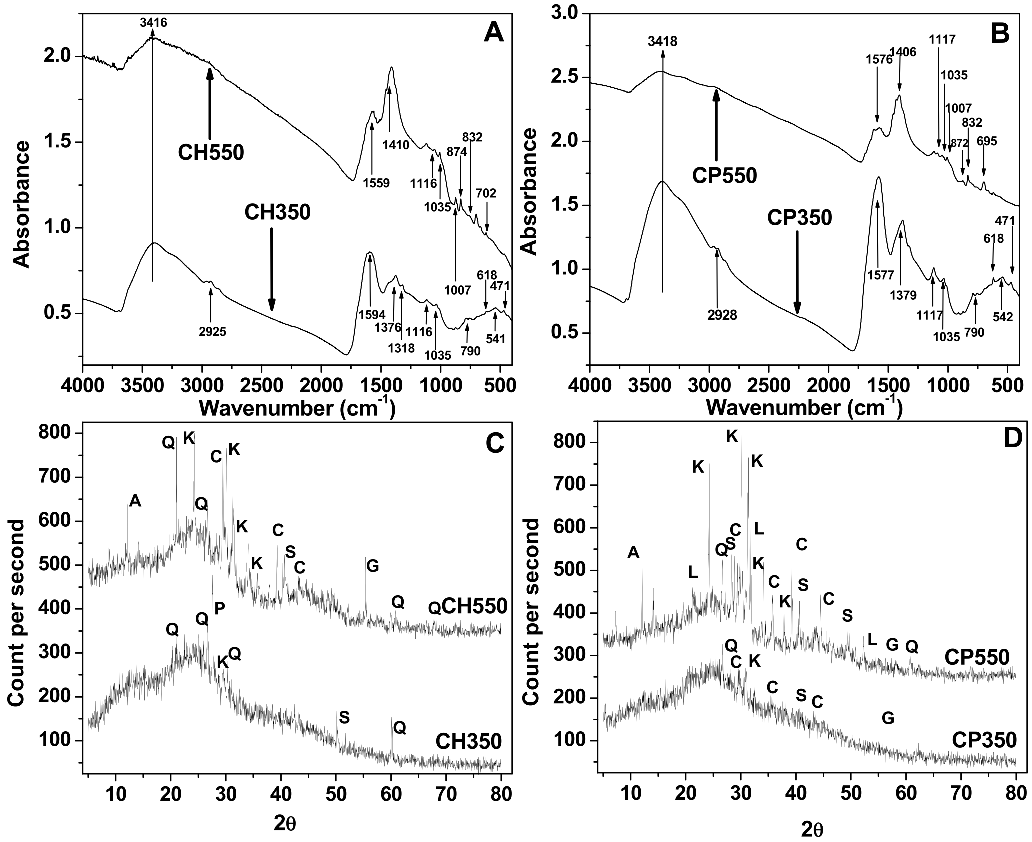

Figure 2. FTIR analysis of (A) CH350 and CH550, (B) CP350 and CP550, XRD spectrum of (C) CH350 and CH550 and (D) CP350 and CP550.

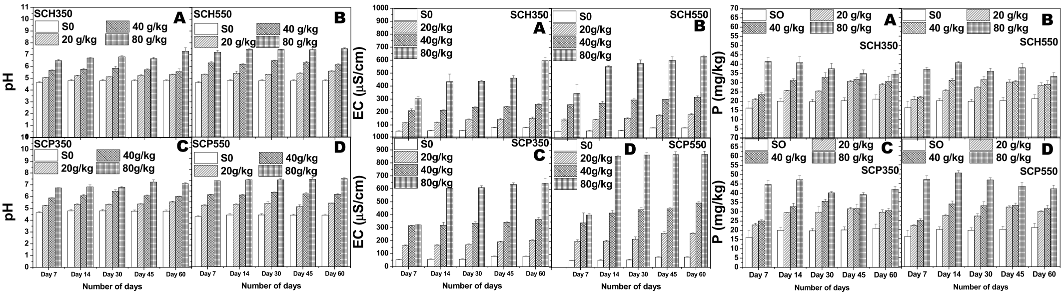

Figure 3. Effect of biochar application rate and incubation time on acidic soil with respond on soil pH (left), electrical conductivity (middle) and available P (right).

Effects of biochar on different soil properties

Soil pH, electrical conductivity and available P

The effect of the number of incubation days and biochar type on soil pH upon amendment of acid soil with biochar is presented in Figure 3. The application of biochar from CH and CP on acid soil had a significant effect ($p < 0.05$) on the increase in soil pH as compared with control. At higher doses (80 g kg^{-1}) CH350 and CP350 had a significant effect on soil pH ($p < 0.05$) while CH550 and

CP550 had no significant effect ($p > 0.05$) on soil pH over incubation time. From Figure 3, an increase in biochar amendment rate for all four biochar, increased the soil pH significantly ($p < 0.05$), with CP550 having the greatest effect. Furthermore, the combined effect of amendment rate and incubation time had a significant effect on the increase in soil pH ($p < 0.05$) for each number of incubation days. The greater sensitivity of soil pH upon addition of CP550 at the start of incubation and then maintaining higher soil pH was previously observed (Martinsen et al. 2015). Thus, CP biochar can be said to be a better liming potential agent as compared to CH biochar due to its greater alkalinity, higher $CaCO_3$eq(%) and a greater acid-neutralizing capacity. Moreover, it should be noted that, after 60 days of incubation, the increase in soil pH with amendment rate (20, 40 and 80 g kg^{-1}) for each biochar were: for CH350; 0.46, 0.81, 2.51 units, for CH550; 0.75, 1.41, 2.71 units, for CP350; 0.68, 1.27, 2.32 units and for CP550; 1.02, 1.95, and 3.3 units as compared with the control. Therefore, the liming effect was in the order CP550 > CH550 > CP350 > CH350. In the same way, studies on the impact of biochar on soil pH have previously been reported (Yuan and Xu 2012; Chintala et al. 2014). The increased soil pH by these biochars can be due to the biochar alkalinity, $CaCO_3$(eq)% content, the presence of silicate, carbonate, and bicarbonate minerals, the presence of negatively charged phenolic, carboxyl and hydroxyl groups on biochar surfaces and acid-neutralizing capacity of the biochar. From biochar analysis, CP biochar had higher biochar alkalinity than coffee husk biochar at the same temperature (Table 1) which reacts with H^+ from the solution, reducing the H^+ ions concentration (Dai et al. 2014). The presence of more silicates, carbonates, and bicarbonates in CP550 than in CH550 makes CP550 a better liming potential material. The lower temperature produced biochars cause an increase in soil pH due to functional groups on the biochar such as $- COO^-$ and $- O^-$ which combines with H^+ and thereby removing it from soil solution (Yuan et al. 2011). In this work, we observed a continuous increase in soil pH until 60 d unlike other work who reported a decline in soil pH during the first 20 d of incubation due to nitrification of NH_4^+-N (Zhao et al. 2015). The continuous increase in pH may be due to a slow release of basic ions from the carbonates and bicarbonates (Yuan et al. 2011) and also due to the buffering capacity of the biochar (Alkalinity of biochar in Figure 1) which can reabsorb the H^+ released during nitrification of NH_4^+-N. From the study, analysis of variance showed that amendment type and incubation time had significant effects ($p < 0.05$) on soil pH only at higher incubation rate for all four biochars. Amendment rate and incubation time had a significant effect ($p < 0.05$) for amendments with CH350, CH550 and CP350 only. The increase in soil pH of acidic soils when incorporated with biochar limit metal toxicity and can also lead to negative effect associated with excessively high pH on crop production (Alburquerque et al. 2014).

Incorporation of all four biochars in soil significantly increased the soil EC ($p < 0.05$) at different incubation days as compared to control (Figure 3). After 7 d of incubation and amendment rate of 20, 40 and 80 g kg^{-1}, the overall increase in soil EC for biochar was in the order CP550 > CH550 > CP350 > CH350 as compared to the control. From 7 d to 14 d, the EC increased drastically for all four biochars before forming a plateau and the increase in soil EC for amendment rate of 80 g kg^{-1} for CP550 was more remarkable. The sharp increase in EC from the 14 d of incubation may be due to the dissolution of low solubility calcite in the biochar due to its reaction with H^+ in the acid soil to release calcium ions and the plateau form the later may be due to the complete dissolution of the calcite. Furthermore, we can note that biochar produced from cocoa pods at 550°C increased EC more remarkably which can be attributed to the presence of sylvite, bicarbonate of potassium on XRD spectra of CP550. After 60 d of incubation, the amended soils at 80 g kg^{-1} presented the highest EC. Besides, previous work had indicated that an increase in soil EC is attributed to alkalinity, $CaCO_3$ equivalence, ash content, and the amount of soluble salts in the incorporated biochar (Cantrell et al. 2012; Singh et al. 2017). Analysis of variance showed that amendment type and amendment rate had a significant effect ($p < 0.05$) on soil EC from 14 d of incubation to 60 d. Also, amendment rate × incubation time, amendment type × incubation time had a significant effect ($p < 0.05$) on soil EC.

The quantity of available P in acidic soil significantly ($p < 0.05$) increased when amended with biochar (Figure 3). During the whole incubation period, a slight increase of available P was observed in the control acidic soil from 16.27 mg kg^{-1} after 7 days to 21.10 mg kg^{-1} after 60 d which can be attributed to P mineralization which occurs when dried soils are rewet (Laboski and Lamb 2003). After 7 d of incubation, the amount of available P increased significantly ($p < 0.05$) into 20, 40 and 80 g kg^{-1} amendments to 23.9%, 40.6%, and 147.5% for CH350, 24.0%, 36.0%, 32.0% for CH550, 37.0%, 49.7% and 167.2% for CP350, and 33.3%, 48.9% and 181.2% for CP550. The increase was in the order CP550 > CP350 > CH350 > CH550. A rise and fall in the amount of available P were observed with increasing incubation time with all four biochar. This rise and fall were dependent on the biochar type and amendment rate. Generally, soil incubated at 20 g kg^{-1} had a longer rising period for available P (averagely 45 d for all four biochars), then followed by an amendment rate of 40 g kg^{-1} whose available P rose with time up to 30 d (except for CP550 at 14 d of incubation time) and the shortest risen time was for amendment rate of 80 g kg^{-1}, which corresponded for 14 d (except for CH350 at 7 d of incubation time). From the above, we can conclude that increasing the rate of biochar, release rapidly available P. On the other hand, the percentage decrease after 60 d of incubation compared to the maximum amount of available P release was for 20, 40 and 60 d was relatively little.

Several works have asserted the inconsistency on the effect of biochar on soil P availability due to the manner in which biochar application affect the P cycle either directly or indirectly through various mechanisms. Manolikaki et al. (2016) reported that biochar from agricultural waste have a potential to be a source of P, and biochar as a modifier of soil pH and ameliorator of P complexing metals (Al^{3+}, Fe^{3+}, Fe^{2+}), and biochar as a promoter of microbial activity (DeLuca et al. 2015). In this work, an increase in the availability of P from soil-biochar mixture could be as a result of direct supply of P from biochar and dissolution of inorganic P in the acid soil. The second phase of incubation time shows a retention of available P after the increase as observed in past research work (Zwetsloot et al. 2016). The reduction in available P may be due to ash minerals and the presence of high $CaCO_3$ equivalent in biochar produced at higher temperature which causes the retention of P through the formation of Ca-P precipitates (Hollister et al. 2013; Wang et al. 2015).

Exchangeable acidity, Al and Fe

Results showing the effect of all four biochars in Ex Ac can be depicted on Figure 4. Compared to control, treatment application of all four biochars decreases drastically exchangeable acidity ($p < 0.05$). After 45 d of incubation time, the amendments 20, 40, and 80 g kg^{-1} led to a significant decrease which was higher for CP550 (89.2%, 95.5% and 98.7% respectively), followed by CH550 (75.6%, 90% and 97.3% respectively), then CP350 (81%, 89.4% and 96.1% respectively) and finally CH350 treatment (60.8%, 87.2% and 95% respectively). Thus, the effect of the different biochars on Ex Ac decreased in the order CP550 > CH550 > CP350 > CH350. There was a significant difference

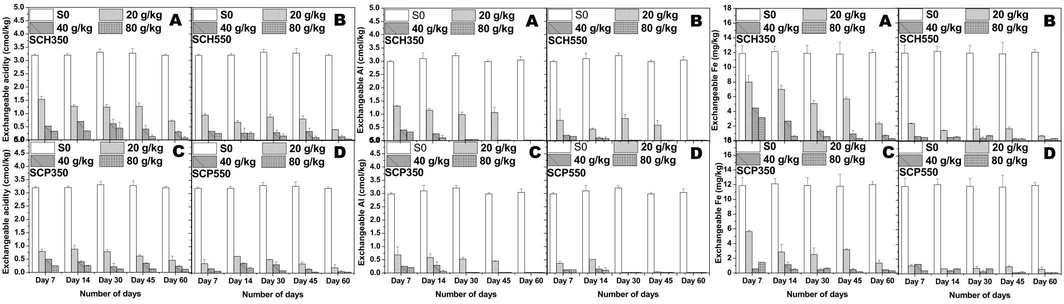

Figure 4. Effect of biochar application rate and incubation time on acidic soil with respond on Exchangeable acidity (left), Exchangeable Aluminium (middle) and Exchangeable Iron (right).

($p < 0.05$) on the effect of soil acidity with application rate of the four biochars, but on the 60th day, application rate had no significant difference ($p > 0.05$) on Ex Ac. Analysis of variance showed the effect of amendment type and incubation time significantly varied ($p < 0.05$). The soil Ex Ac at all biochar dosage for all four biochar and the effect of amendment rate and incubation time on soil Ex Ac had a significant effect on it variation ($p < 0.05$) for CH350, CH550, and CP350 while for CP550 there was no significant difference during treatment ($p > 0.05$).

Acid soil treated with all four biochars decreased significantly Ex Al and Fe significantly ($p < 0.05$). The decrease was very rapid after 7 d of incubation then decreased slowly to its minimum value. As can be depicted from the Figure 4, the order of alleviation of Al and Fe by the different biochar treatment is in the order CP550 > CH550 > CP350 > CH350. Incubation time had a significant effect ($p < 0.05$) on the amount of Ex Al and Fe with biochar type and amendment rate from the study, analysis of variance showed the effect of amendment type and incubation time had a significant effect ($p < 0.05$) on soil Ex Al and Fe at all biochar dosage. For all the four biochars, amendment rate and incubation time had a significant effect ($p < 0.05$) on soil Ex Al and Ex Fe for CH350, CH550, and CP350 and was not influence significantly ($p > 0.05$) with CP550. The major ions concern in this exchangeable medium are the H^+, Al^{3+}, Fe^{2+}, and Fe^{3+}. The mechanism in their reduction in soil solution involves precipitation of the metallic ions by alkaline oxides, carbonates, and silicates in the biochar, complexation with organic functional groups (e.g. – O, – OH, – COOH) (Qian et al. 2013). CP550 had the highest liming potential, acid-neutralizing capacity, biochar alkalinity and contain many basic minerals which can relate to its ability to have a greater reduction in Ex Ac, Al and Fe. Recent works of the application of biochar into soils and its effect on soil acidity and Ex Al and Fe asserted the same observation (Chintala et al. 2014; Dume et al. 2017).

Soil organic carbon (SOC)

All four biochar amended soils had significantly higher SOC ($p < 0.05$) than the control throughout the incubation time (Figure 5). It is observed that application of biochar produced at lower temperature increases SOC proportionally with increase in amendment rate. After 30 d of incubation, the highest SOC was observed. In the soil amended with biochar of 20, 40 and 50 g kg^{-1}, the increase in SOC as compared to the control were 2.7, 2.6, and 3.2 times for CH350, 1.99, 1.97, and 2.1 for CH550, 2.5, 2.6, and 3.6-fold for CP350 and lastly 2.1, 2.4 and 3.04 for CP550 respectively. Also, the increase in SOC was more pronounced when amended with cocoa pods biochar than coffee husk biochar. From 30 d to 60 d of incubation, a decrease in SOC was observed and the decrease was more pronounced in biochar produced at lower temperature as compared to those produced at higher temperature. An increase or a decrease in SOC in soils can be due to negative or positive priming effect of biochar with incubation time. Increase in soil organic carbon is due to the presence of recalcitrant carbon (Nyambo et al. 2018) and decrease in the mineralization of the soil carbon due to sorption of labile soil organic matter onto the biochar particles (Singh and Cowie 2014) and/or a very short-term inhibitory effect of microbial activity of biochar–associated volatile organic compounds (Spokas et al. 2011). The decrease in SOC after 30 d may be due to remains of labile organic material remaining in the pyrolyze biochar (Luo et al. 2011) which in turn activate soil microorganisms.

Analysis of Pearson correlation coefficient between soil properties after amendments

From Table 2, Pearson correlation reveal that, increase in soil pH had a positive significant correlation ($p < 0.05$) when incorporated with CH350, CH550 and CP350 at 20, 40, and 80 g kg^{-1} with incubation time, but for CP550, positive significant correlation ($p < 0.05$) occurred only at high amendment rate ($r = 0.938$). Also, there is a positive significant correlation between soil pH and Soil EC and available P for all four biochars at different amendment rate. Moreover, there is a significant negative correlation of soil pH with Ex Ac, Al and Fe for all four biochars amendment rates. Soil EC had

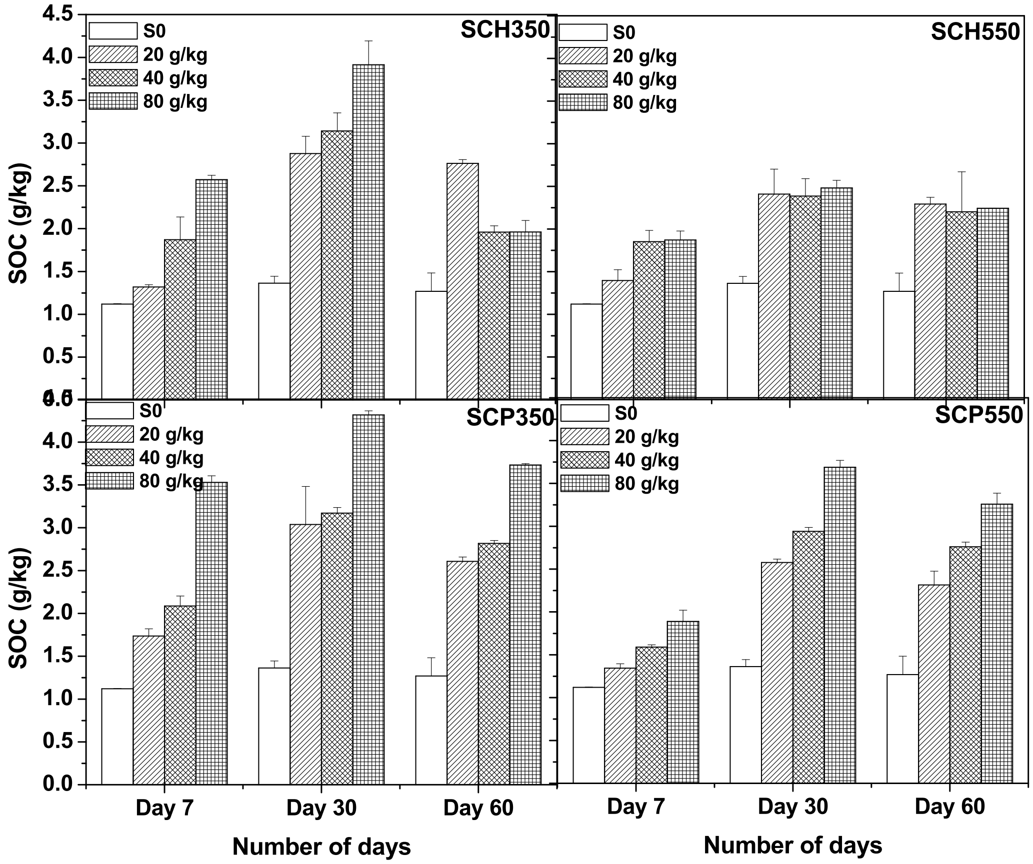

Figure 5. Effect of biochar application rate and incubation time on acidic soil with soil organic carbon.

a positive significant ($p < 0.05$) correlation for all four biochar, irrespective of the amendment rates and incubation days. Furthermore, Soil EC had a positive significant correlation with available P, except at the highest dosage, whereas, negative significant correlations between soil EC and Ex Ac, Al and Fe in all incubation systems were obtained. Available P had a significant positive correlation coefficient with number of incubation days for all four biochars amended at 20 and 40 g kg^{-1}. On the contrary, a negative significant correlation was observed at higher doses. In the same line, available P had a significant negative correlation with Ex Ac, Al, and Fe for all four biochar at 20 and 40 g kg^{-1} dosage was computed. Meanwhile at 80 g kg^{-1}, the correlation is significantly positive. In the case of Ex Al and Fe, all four biochar and their amendment rate had significant ($p < 0.05$) negative correlation with incubation time. A positive correlation of soil pH with incubation time is due to the slow release or dissolution of calcite from the biochar and the buffer properties of the biochar, thus causing a progressive increase in soil pH and a negative correlation with exchangeable acidity, Al, and Fe due to the precipitation of these exchangeable's. Similar to previous studies (Zhao et al. 2015), biochar amendments significantly improve soil pH and decreases exchangeable Al and acidity. A positive correlation in soil ECs with number of days is linked to slow dissolution of the basic compounds in the biochar to release soluble ions responsible for the soil EC. The positive correlation with available P may be due to the addition of P from the biochar, thus enhancing P, whereas the negative correlation at 80 g kg^{-1} may be due to the saturation of the soil solution with soluble basic cations and available P which leads to the precipitation of phosphate as describe by (Hollister et al. 2013). The antagonistic effect of available P with Ex Ac, Al and Fe is well known. It is due to the exchange

Table 2. Pearson's correlation coefficients for the relationships between incubation time (Days), soil pH (pH), soil EC (EC), available P (Avail P), Exchangeable Acidity (Ex Ac), exchangeable Aluminium (Ex Al) and exchangeable Iron (Ex Fe) on the amended soils at different rates.

SCH350										SCH550							
20 g/kg		Days	pH	EC	Avail P	Ex Ac	Ex Al	Ex Fe	20 g/kg	Days	Days	pH	EC	Avail P	Ex Ac	Ex Al	Ex Fe
	Days	1	0.841	0.954	0.847	−0.859	−0.841	−0.923			1	0.702	0.974	0.828	−0.693	−0.649	−0.781
	pH		1	0.670	0.841	−0.571	−0.589	−0.789		pH		1	0.615	0.370	−0.978	−0.981	−0.887
	EC			1	0.773	−0.766	−0.753	−0.907		EC			1	0.831	−0.593	−0.586	−0.658
	Avail P				1	−0.633	−0.519	−0.659		Avail P				1	−0.462	−0.384	−0.650
40 g/kg	Days	1	0.831	0.982	0.547	−0.801	−0.882	−0.893	40 g/kg	Days	1	0.737	0.978	0.426	−0.659	−0.833	−0.966
	pH		1	0.803	0.386	−0.748	−0.597	−0.850		pH		1	0.833	0.156	−0.546	−0.780	−0.837
	EC			1	0.555	−0.759	−0.900	−0.894		EC			1	0.554	−0.649	−0.915	−0.989
	Avail P				1	0.048	−0.824	−0.859		Avail P				1	−0.276	−0.818	−0.633
80 g/kg	Days	1	0.802	0.902	−0.973	−0.764	−0.787	−0.705	80 g/kg	Days	1	0.738	0.798	−0.676	−0.988	−0.826	−0.522
	pH		1	0.927	−0.661	−0.738	−0.843	−0.603		pH		1	0.976	−0.247	−0.666	−0.896	−0.100
	EC			1	−0.809	−0.646	−0.837	−0.821		EC			1	−0.239	−0.749	−0.956	−0.191
	Avail P				1	0.704	0.809	0.712		Avail P				1	0.713	0.361	0.156
SCP350									SCP550								
20 g/kg	Days	1	0.899	0.958	0.675	−0.921	−0.912	−0.772	20 g/kg	Days	1	0.194	0.955	0.794	−0.663	−0.818	−0.448
	pH		1	0.877	0.692	−0.775	−0.951	−0.926		pH		1	−0.010	−0.165	0.010	−0.157	−0.769
	EC			1	0.562	−0.958	−0.925	−0.669		EC			1	0.828	−0.714	−0.770	−0.212
	Avail P				1	−0.354	−0.476	−0.822		Avail P				1	−0.202	−0.563	−0.384
40 g/kg	Days	1	0.852	0.986	0.316	−0.765	−0.848	−0.560	40 g/kg	Days	1	0.264	0.910	0.427	−0.611	−0.838	−0.774
	pH		1	0.823	0.378	−0.710	−0.484	−0.885		pH		1	0.829	0.297	−0.593	−0.701	−0.877
	EC			1	0.258	−0.776	−0.817	−0.577		EC			1	0.722	−0.247	−0.722	−0.939
	Avail P				1	−0.736	−0.441	0.080		Avail P				1	0.406	−0.314	−0.901
80 g/kg	Days	1	0.814	0.706	−0.648	−0.877	−0.749	−0.762	80 g/kg	Days	1	0.939	0.640	−0.872	−0.670	−0.876	−0.679
	pH		1	0.429	−0.519	−0.594	−0.431	−0.623		pH		1	0.772	−0.677	−0.382	−0.751	−0.545
	EC			1	−0.390	−0.642	−0.983	−0.966		EC			1	−0.207	0.043	−0.705	0.028
	Avail P				1	0.901	0.534	0.419		Avail P				1	0.932	0.735	0.874

* Coefficients that are significant ($p < 0.05$) are shown in bold text.

reaction of Al and Fe with the alkaline from biochar and the functional groups (-O^- and – COO^-) with the biochar and liberating phosphate and also the provision of P into the soil solution as biochar plays the role of P provider.

Conclusion

The objective of this study was to evaluate the effects of biochar rate and incubation time on soil chemical properties gave the following main findings: (i) increase in biochar rate and incubation time for all four biochar, effectively alleviate the soil acidity by yielding an increase in soil pH, soil EC and a drastic drop in exchangeable acidity, exchangeable Al and Fe. CP550 caused the greatest increase in soil pH; (ii) the fertility aspect of the biochar was demonstrated with the increase in available P upon addition of biochar. Available P increased with biochar rate and incubation time. It was observed a read sorption of P at higher dosage with increasing incubation time; (iv) biochar amendment increased SOC. Increase then a decrease in SOC was more pronounced with biochar produced at lower temperature. The effect of biochar on these soil chemical properties was mainly due to the intrinsic chemical properties of the biochar such as biochar alkalinity, acid-neutralising capacity, $CaCO_3$eq(%), presence of basic inorganic minerals, presence of complexing functional groups and P availability. Thus, clear knowledge liming and fertilizing properties of biochar and its effect on soil properties is useful. Thus, biochar can play the dual role of a liming agent and a source of P fertilizer nutrients. Implementing these types of studies with different biochar obtain from these localities and testing it beneficial agricultural amendments value on their soils, will help to design biochars for farmers in these localities.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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RESEARCH ARTICLE

Effect of coffee husk and cocoa pods biochar on phosphorus fixation and release processes in acid soils from West Cameroon

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Abstract

Acid soil in West Cameroon has limited phosphorus (P) availability which limits plant growth. This is mainly because of low pH, high levels of exchangeable aluminium (Al) and iron (Fe) and fixation of P. In this study, acid soils, sampled in Bafang, were amended with biochar produced from coffee husks (CH) and cocoa pod husks (CP) at two different temperatures (350 and 550 °C) in other to evaluate the effect on the physicochemical properties of the acid soil and the effect on P sorption and desorption. The soil was amended with biochar at a rate of 0, 20, 40 and 80 g/kg and incubated for 7 and 60 days. Physicochemical properties of all soil–biochar samples were determined followed by sorption experiments and data fitted in the Langmuir and Freundlich isotherm models in other to evaluate soil P sorption capacity and its affinity to soil amended with biochar. Moreover, desorption studies were done to evaluate the availability of P in soil amended with biochar after sorption. The outcomes of this study reveal an increase in soil pH, electrical conductivity (EC), available P, soil organic carbon and a drastic decrease in exchangeable Al and Fe. The point of zero charge of biochar-amended soil was higher than the control and increased with amendment rate. The experimental data of the sorption of P on soils and soil–biochar samples fits into Langmuir and Freundlich models ($R^2 > 0.9$) suggesting that the P adsorption is controlled by both model mechanisms. Soil–biochar mixture results in a decrease in the sorption capacity as compared with the control and the decrease was predominant with increasing amendment rate. At amendment rates of 20, 40 and 80 g/kg after 7 days of incubation, Q_{max} for SCH350 were 2267, 2048 and 1823 mg/kg which increased to 2407, 2112 and 1990 mg/kg after 60 days of incubation. This tendency was observed for all biochar inputs with respect to the increase in incubation days. Furthermore, desorption of P from soil–biochar mixtures was enhanced with biochar added at greater rate and produced at higher temperature. The desorption percentage was increased by more than around 10% for all biochar types from 20 mg/kg to 80 mg/kg amendment. Thus, biochar addition to acid soils reduces P fixation to acid soil and improves P desorption to soil solution, thereby providing more available P in the soil solution and better conditions for plant growth.

KEYWORDS

acid soil, biochar, phosphorus, sorption

1 | INTRODUCTION

Tropical soils in Africa are mostly acidic (Takow et al., 1991) and acidic soils are widely spread in the western region of Cameroon (Tematio et al., 2004) which presents critical levels of P (Tchuenteu, 1997). This is because of a high level of fixation via reaction with hydr(oxides) of Al and Fe found in clay minerals thus depriving P to plants resulting in poor growth (Mbene et al., 2017; Yadav et al., 2012). The fixation of P in soils is influenced by soil organic matter, pH, exchangeable Al, Fe, amount and type of silicate clays, calcium carbonate content (Eriksson et al., 2015; Gérard, 2016; Guppy et al., 2005) which affect soil biogeochemical processes (dissolution, adsorption and precipitation). Generally, acid soils manifest a dominance in H^+ and Al^{3+} ions in their soil solution (Ondo, 2011), little organic matter content because of mineralisation (Tiessen et al., 1994) and lack of nutrients. One of the ways to remediate these limitations is amendments which include the application of lime (Pagani & Mallarino, 2012), compost (Chen et al., 2004), wood ash (Nkana et al., 2002), direct P fertilization (Ondo et al., 2017), rock phosphate (Basak & Biswas, 2016), etc. Excess use of P fertilizer and manure may constitute a risk of surface- and ground water impairment known as eutrophication (Parvage et al., 2013). Excess liming will lead to soil compaction (Alavéz-Ramírez et al., 2012). An alternative to these materials is the use of biochar.

Biochar has received great attention as an alternative option to overcome many aspects of soil limitations. This is a material derived from the pyrolysis of biomass in an atmosphere containing little or no oxygen (Joseph & Lehmann, 2009). Biochar has multifunctional values that includes the use of it for the following purposes: soil amendment to improve soil health, nutrient addition, immobilizing agent for remediation of toxic metals and organic contaminants in soil and water and mitigation of greenhouse gas emissions (Abhishek et al., 2022). It is also used in the domain of carbon sequestration, climate change mitigation and as a soil conditioner (Bolan et al., 2022). Feedstocks used for the production of biochars are mostly obtained from agricultural biomass, which is abundant and of little cost. Coffee and cocoa are one of the main cash crops grown in Cameroon. Waste produced from these crops (coffee husk and cocoa pod husk) when poorly disposed of can generate serious environmental problems. In Bafang, coffee husks are disposed of in the river which can cause siltation of rivers (Acchar & Dultra, 2015) and poor disposal of cocoa pod husks in cocoa farms can be source of black pot rot to plants (Yapo et al., 2013). Thus there is a need to properly manage these materials to protect the environment.

Biochar application to acid soils alters soil physicochemical properties (Chintala, Mollinedo, et al., 2014) and improves P availability (Glaser & Lehr, 2019). Biochar addition ameliorates soil acidity because of its alkaline nature by reducing the quantity of H^+, Al^{3+}, Fe^{3+} and Fe^{2+} and thus reducing P precipitation (Wang et al., 2012). Earlier studies have reported that biochar produced from different feedstocks and pyrolysis temperatures has diverse physical and chemical properties such as functional groups, mineral contents, pH, $CaCO_3$ content, cation exchange capacity and surface area (Chintala, Schumacher, et al., 2014; Eduah et al., 2019; Liang et al., 2014). Moreover, biochar added to acid soils have contrasting results on the fixation of P through sorption studies. Some results have presented an increase in sorption of P over the control acid soils because of the binding of phosphate to the carbonates and oxides of Ca and Mg (Novak et al., 2009; Xu et al., 2014; Zhang et al., 2016) while on the contrary, less sorption of P was also observed than the control acid soils which was attributed to the precipitation of Al^{3+} and Fe^{3+} (DeLuca et al., 2015) and the repulsion of the negative phosphate ions by the negative charge of biochar (Chintala, Schumacher, et al., 2014; Martínez et al., 2017).

Few research works have been done to observe the changes in the physicochemical properties of biochar-amended soil (Djousse Kanouo et al., 2019; Pouangam Ngalani et al., 2022) in Cameroon and to our knowledge, none on how P fixation is affected by biochar amendment on acid soils from west Cameroon. The present study had the objectives to (i) find out the effect of CH and CP biochar on the physicochemical properties of acid soil at different amendment rates and incubation times and (ii) the effect of biochar on P sorption and desorption.

2 | MATERIALS AND METHODS

2.1 | Soil sampling and biochar preparation

Soil samples were randomly collected at a depth of 15 cm on a 2-hectare cocoa and coffee farm in Bafang (5°08′55″N 10°09′32″E), West region of Cameroon. The soil samples were air-dried for 1 week, crushed, sieved through a 2-mm sieve and stored in plastic bags for incubation studies. The soil was a Loamy soil with 42.9% silt, 33.3% sand and 23.8% clay. It was acidic with a pH of 4.7, and electrical conductivity of 53.2 μS/cm, exchangeable acidity of 3.1 cmol/kg and available P of 16.1 mg/kg.

Coffee husks and cocoa pod husks collected from coffee processing factories and cocoa farms in Bafang, were washed with tap water and rinsed with distilled water, dried at 105°C to remove moisture then ground and sieved with a 2-mm sieve. The biomass was then inserted in the muffle furnace set up at two different temperatures (350°C and 550°C) for 4 h and herein annotated as CH350, CH550, CP350 and CP550 respectively. Thereafter, the biochars were finely ground, dried (105°C) and stored in polythene bags for characterization and incubation experiments. This preparation process was proposed by (Pouangam Ngalani et al., 2022).

2.2 | Incubation study for soil–biochar

An incubation pot-experiment study was done to investigate the effect of different biochar at varying pyrolysis temperatures, amendment rates and incubation periods on the physicochemical properties of the acid soil sample and P sorption and desorption capacity. The soil was mixed in transparent incubation plastic pots with CH350, CH550, CP350 and CP550 at the rate of 0 g/kg, 20 g/kg, 40 g/kg and 80 g/kg then incubated for 7 and 60 days. Each treatment was replicated four times at 70% field water capacity and left at room temperature. At the end of the incubation periods, the amended and the control soil samples were air-dried, ground and sieved to <2 mm and then stored in plastic cups for characterization and P sorption and desorption studies. Soil–biochar mixtures were labelled as SCH350, SCH550, SCP350 and SCP550 for soil incubated with biochar pyrolysed at 350 and 550°C.

2.2.1 | Characterization of biochar, soil and soil–biochar samples

The ash content of the biochar was determined by dry combustion of the biochar in a muffle furnace at 750°C for 6 h (Rehrah et al., 2014). The acid-neutralizing capacity of biochar was determined by mixing biochar in a solution of HCl and back titrating with NaOH (Martinsen et al., 2015) and $CaCO_3$ equivalence was determine by Rayment and Lyons (2011) method. Fourier transform infrared spectroscopy (scan range from 400 to 4000 cm^{-1}) was recorded on an Alpha spectrometer from Bruker Optics and XRD patterns of the biochar were registered with CuKα (2θ from 5 to 80°) for 7 h using Bruker D4. The surface morphology and the elucidation of the chemical properties of the various biochar were investigated by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). The samples were coated with 10 nm gold layer using the rotary pump sputter coater (Leica EM ACE600, Wetzaler, Germany). The coated samples were loaded on the ThermoScientific Prisma E SEM with an Oxford EDS system for SEM-EDS. These observations were operated at an accelerated potential of 20.00 KeV and magnifications of SEM images at magnification 1000× and 3500× taken. Biochar pH and EC were determined by shaking a mixture of biochar to deionized water (1:5 wt/wt ratio) (Singh et al., 2010) while the pH and EC of soil and soil–biochar mixtures were determined by shaking water and deionized water in the ratios 1:2.5 and 1:5 respectively (Pansu & Gautheyrou, 2007). Available P from biochar, soil and soil–biochar were determined using the Olsen P solution (0.5 M $NaHCO_3$ at pH 8.5) and the aliquot taken for P Spectro colorimetry determination (Murphy & Riley, 1962; Olsen et al., 1954). Quantification of organic carbon from biochar, soil and soil–biochar mixture was determined by Walkley and Black (1934) method. Exchangeable acidity, exchangeable Al (Ex Al) and exchangeable Fe (Ex Fe) were based on the principle of sample washing with a saline solution of 1 M KCl solution (Pansu & Gautheyrou, 2007). Exchangeable acidity, in the aliquot was determined by titrating against 0.01 M NaOH with phenolphthalein as an indicator then for Ex Al, after adding 1 M KF to the former solution, the pink solution was titrated to colourless using 0.01 M HCl. Ex Fe was determined by analysing an aliquot of solution by complexation of Fe^{2+} with ortho-phenanthroline and the absorbance read with visible-spectroscopy.

2.3 | Point of zero charge analysis of soil and soil–biochar mixtures

The salt addition method was used for the determination of the point of zero charge (PZC) (Bakatula et al., 2018). 0.2 g of soil and soil–biochar mixture was added to a series of 25 mL tubes containing 15 mL of 0.05 M $NaNO_3$ solution whose pH (pH_i) was adjusted in the range 2, 3, 4, 5, 6, 7, 8, 9 and 10 with 0.1 M HNO_3 and 0.1 M NaOH. The tubes were agitated for 24 h on a head-on agitator at 200 rpm, then left to settle. The pH (pH_f) of the supernatant in each tube was then measured. The PZC were obtained after plotting a graph of pH_f-pH_i against pH_i, that is, at the pH at which the curves cuts the pH_i axis.

2.3.1 | Sorption phosphorus study experiment soil–biochar samples

To determine sorption characteristics, related to soil–biochar properties and elucidate the mechanisms involved in sorption, the following experiments were performed. In this study, 0.2 g of each sample was mixed with 10 mL of KH_2PO_4 solution containing 0, 5, 10, 20, 80, 160, 320 and 480 mg/L P and 0.01 M KCl as background electrolyte in 25 mL centrifuge tubes. Then two drops of chloroform were added in each sample to act as microbial growth inhibitor. The tubes were set on an end-end shaker for 16 h at 150 turns per minute. At the end of the shaking process, the samples were centrifuged at 5000 rpm for 10 minutes then filter through a Whatman No.5 filter paper to obtain a clear extract. The clear extracts were analysed for available P following Murphy and Riley (1962). Each adsorption process was done in quadruplets. The quantity of P adsorbed at equilibrium by treated soil samples was calculated using equation (1) below

$$Q_e = \frac{(C_i - C_e)\ x\ V}{m} \tag{1}$$

Where Q_e (mg/kg) is the quantity of P adsorbed by treated soil samples, C_i (mg/L) the initial concentration of P, C_e (mg/L) the quantity of P at equilibrium after adsorption, V (L) the volume of P solution used for adsorption and m (kg) the mass of amended soil sample.

The experimental data of the quantity of P adsorbed at equilibrium were fitted into two important isotherm models namely Langmuir and Freundlich. Each isotherm is characterized by definite constants whose values express the surface properties and affinity of the amended soil samples. The nonlinear form of Langmuir isotherm model used is represented by equation (2) which describes single-layer adsorption:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

Where, Q_e (mg/kg) is the quantity of P adsorbed by the soil or soil/biochar mixture, C_e (mg/L) the quantity of P at equilibrium after adsorption, Q_{max} the P adsorption maximum for Langmuir model (mg/kg), K_L the equilibrium constant that determines the binding energy (L/kg), the higher the K_L the stronger the binding force.

The nonlinear form of Freundlich is given in equation (3) below which describes multi-layer adsorption

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

Where Q_e (mg/kg) is the quantity of P adsorbed by the soil or soil/biochar mixture, C_e (mg/L) the quantity of P at equilibrium after adsorption, K_F (mg/kg) the Freundlich constant indicating adsorption capacity not specifically the maximum adsorption capacity, and $\frac{1}{n}$ the adsorption intensity which indicates the heterogeneity of the material (Cucarella & Renman, 2009).

2.3.2 | The desorption of phosphorus experiment

In order to evaluate the reversibility of phosphate sorbed onto soil and soil/biochar mixtures, their desorption characteristics were also determined. In the first phase, 10 mL of 80 mg/L of P was shaken with 0.2 g of soil or soil/biochar mixture for 16 h on an end-to-end shaker. At the end of the sorption experiment, the supernatant was removed; the amended soil samples were obtained as the residue and dried at room temperature. Then in the second phase, the desorption experiment of P from the amended soil samples from the dried residue was done in the following way, 0.1 g of the soil and soil/biochar was mixed with 10 mL of 0.01 KCl and agitated for 16 h, then centrifuged and the supernatant was analysed for the determination of P (Murphy & Riley, 1962). The desorption percentage was calculated using equation (4) below:

$$\text{Desorption percentage}\ (\%) = \frac{P_{\text{desorbed}}}{P_{\text{sorbed}}} x100 \tag{4}$$

Where, P_{sorbed}(mg/kg), is the quantity of P adsorbed at equilibrium and P_{desorbed} (mg/kg) is the quantity of P desorbed.

2.3.3 | Statistical analysis

Nonlinear regression analysis was used to fit Langmuir and Freundlich isothermal equations to data. Curve fitting and Statistical analyses were done using Origin 8.5. The goodness of fit was evaluated based on coefficient of determination (R^2). The significant difference between the factors means for parameters under analysis were determined at a 5% level of significance ($\alpha = .05$).

3 | RESULTS AND DISCUSSION

3.1 | Properties of biochar, soil and soil–biochar mixture

3.1.1 | Biochar

Properties of biochar are well discussed in our previous work (Pouangam Ngalani et al., 2022). In summary, biochar characterizations reveal that its properties depend on the biomass type and pyrolysis temperature. Biochar produced from cocoa pod husk had a greater liming potential as compared with coffee husk and the trend increases with pyrolysis temperature. All four biochars had pH above 9 and a large ash content because of the presence of calcite, kalinite and quartz. The acid-neutralizing capacity of CP biochar was significantly ($p < .05$) more than that of CH biochar irrespective of pyrolysis temperature. So we can hypothesize a greater H^+ consumption by CP biochar in acid soils as compared with CH biochar pyrolysed at the same temperature. Available P is greater in biochar produced from CP than that produced from CH irrespective of pyrolysis temperature.

Scanning electron microscopy images of biochars produced at 350 and 550°C are shown in Figure 1 at two different magnifications (2000 and 3500). The biochars displayed a heterogeneous surface morphology and a complex structure. The structure presented cracks, pores and crevices with irregular forms, randomly distributed and of different diameters. Biochar produced at 550 °C has rougher surfaces because of the presence of white particles resulting from the accumulation of minerals formed at higher temperatures. Pores on CP biochar were more regular in size as compared with CH because of the greater crystallinity of CP biochar. The presence of pores, cracks and crevices has possible effects on soil water retention, rooting patterns, soil aeration, nutrients sorption and habitat for soil biota (DeLuca et al., 2015; Lehmann et al., 2011; Sheng & Zhu, 2018).

The SEM analysis was coupled with EDX analyses for chemical mapping of elements in different biochar samples and results obtained are presented in Table 1. In Table 1, we observe an increase in C content and reduction in O with increasing pyrolysis temperature. The O/C ratio as determined with SEM–EDX decreases with rising pyrolysis production temperature of the biochar. This result is an accordance with previous results summarized in a review by Ahmed et al. (2016). Other elements present were P, Mg and Ca whose presence in biochars makes them a potential for liming (Chintala, Schumacher, et al., 2014). The presence of indium (in large amounts) may be because it is a trace element found in the soil, especially unpolluted soil, that can be absorbed into plants and hence food chain (Adeniyi et al., 2019).

3.1.2 | Physicochemical properties of amended soil samples

From Table 2, after 7 days of incubation, CH350, CH550, CP350 and CP550 at rate of 0, 20, 40 and 80 g/kg raised the soil pH from 4.7 to 5.1, 5.7 and 6.5; 5.4, 6.3 and 6.5; 5.2, 5.9 and 6.7; 5.7, 6.7 and 7.9 respectively. Also, after 60 days of incubation, CH350, CH550, CP350 and CP550 at rates of 20, 40 and 80 g/kg raised the soil pH from 4.7 to 5.3, 5.6 and 7.3; 5.6, 6.2 and 7.5; 5.5, 6.0 and 7.1; 5.9, 6.7 and 8.2 respectively. It was observed that an increment in soil pH rises from 7 days to 60 days. Moreover, the pH of soil–biochar mixtures increased with rising in pyrolysis temperature and with biochar application rate with CP having the greater impact compared with CH. The application of biochar on soil had a significant effect ($p < .05$) in increasing the soil pH. Soil pH increases because of addition of biochar, were attributed to increased, $CaCO_{3(eq)\%}$ content and acid-neutralizing capacity of the biochar. The presence of silicate, carbonate, and bicarbonate minerals and negatively charged phenolic, carboxyl and hydroxyl groups on biochar surfaces also increased pH. At higher temperature, the silicates, carbonates and bicarbonates are mostly the cause of elevation in pH while at low-temperature produced biochar, the basic functional groups on the biochar such as –COO- and –O- are responsible (Yuan et al., 2011).

An increase in EC was observed to be greater in soil–biochar mixed with CP than CH for the same amendment rate and pyrolysis temperature. Details from Table 2 indicates that, after 7 days of incubation with 20, 40 and 80 g/kg amendments soil EC increased to 116, 211 and 303 μScm^{-1} for CH350, 141, 258 and 345 μS/cm for CH550, 162, 317, 321 μS/cm for CP350 and finally 200, 343 then 403 μS/cm for CP550 respectively as compared with control. This increase was in the order CP550 > CH550 > CP350 > CH350. Moreover, from 7 to 60 days of incubation, CH350, CH550, CP350 and CP550 at rates of 20, 40 and 80 g/kg increased the soil EC to 151, 259 and 596; 181, 317 and 630; 204, 364 and 642; 263, 496 and 872 respectively. The sharp increase in EC from the 7th to the 60th day of incubation is because of the dissolution of kalicinite and calcite by reaction with H^+ in the acid soil solution to release calcium and potassium ions.

The application of biochar to acid soil samples resulted in an increase in available P as compared with the control. After 7 days of incubation, CH350, CH550, CP350 and CP550 at the amendment rates of 20, 40 and 80 g/kg raised the available P by 23.9%, 40.6% and 147.5%; 24.0%, 36.0% and 32.0%; 37.0%, 49.7% and 167.2% and 33.3%, 48.9% and 181.2% respectively. The increase was in the order CP550 > CP350 > CH350 > CH550. From 7 to 60 days of incubation, at an amendment rate of 20

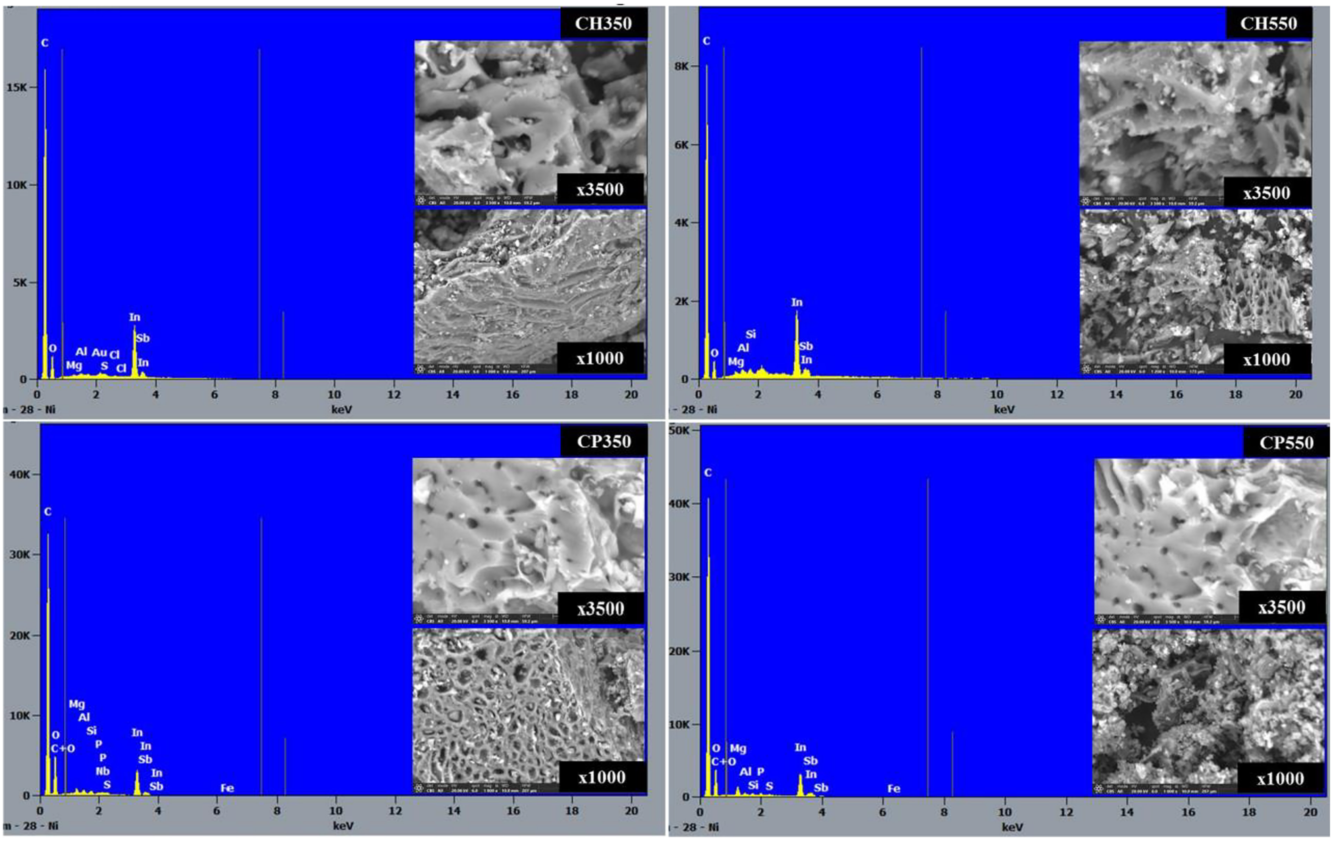

FIGURE 1 Scanning electron micrographs and energy dispersive spectroscopy curves of biochars from CH and CP pyrolysed at 350 and 550°C.

TABLE 1 Elemental compositions (%) obtain from SEM-EDS analysis and the O/C ratio.

Sample	C	O	P	Mg	Cl	Si	Al	Fe	Nb	In	S	Sb	Au	O/C
CH350	47.87	20.05	/	0.18	0.09	/	0.24	/	/	26.77	0.25	3.87	0.69	0.42
CH550	43.87	17.39	/	0.39	/	0.51	0.60	/	/	32.42	/	4.83	/	0.40
CP350	47.96	31.93	0.32	0.85	/	0.38	0.50	0.12	0.75	14.82	0.12	2.24	/	0.70
CP550	55.08	25.72	0.27	1.36	/	0.23	0.25	0.09	/	14.45	0.16	2.40	/	0.47

and 40 g/kg, an increase in available P was observed; which can be attributed to; biochar as a source of soluble P, its reaction with complexing metals (Al^{3+}, $Fe^{3+}$and Fe^{2+}), releasing P and promotion of microbial activity. Whereas, at 80 g/kg, a decreases in available P was observed which could be due to the formation of Ca-P precipitates attributed to the presence of $CaCO_3$ found in the large amounts of ash minerals in the biochar (Hollister et al., 2013; Wang et al., 2015).

A marked decrease in exchangeable acidity, Ex Al and Fe was observed with incubation time (Table 2). With respect to exchangeable acidity, after 60 days of incubation the amendment rate of 20, 40 and 80 g/kg led to a significant decrease which was greater for CP550 (93.4%, 98.1% and 98.8%), followed by CH550 (87.8%, 96.2% and 98.7%), then CP350 (85.6%, 92.8% and 96.2%) and finally CH350 (77.4%, 90.3% and 97.5%). After 7 days of incubation, the drop in Ex acidity, Ex Al and Fe from the application of biochar was in the order CP550 > CH550 > CP350 > CH350. The increase in amendment rate, had a significant drop in Ex Acidity, Ex Al and Ex Fe in the acid soil sample. The cause of reduction can be attributed to the precipitation of the metallic ions by alkaline oxides, carbonates and silicates in the biochar and complexation with organic functional groups (Qian et al., 2013). Recent studies of the application of biochar to soils and its effect on soil acidity and Ex Al and Fe made the same observation (Chintala, Mollinedo, et al., 2014; Dume, Ayele, et al., 2017).

An increase in SOC in soil amended with biochar was observed as compared with the control (Table 2). The increase in SOC increased with incubation time and amendment rate. Elevation in the amount of SOC was more

TABLE 2 Physicochemical properties of soil and soil–biochar mixture after amending for 7 and 60 days.

Days	Soil–biochar mixture	Amendment rate	pH	EC (μS/cm)	Avai. P (mg/kg)	Ex acidity (cmol(H^+)/kg	Ex Al (mg/kg)	Ex Fe (mg/kg)	SOC (mg/kg)
7	S0	0	4.70 ± 0.01	53.20 ± 2.12	16.10 ± 3.43	3.05 ± 0.05	2.985 ± 0.048	11.87 ± 1.09	1.12 ± 0.01
	SCH350	20	5.05 ± 0.01	116.25 ± 2.50	20.73 ± 0.69	1.54 ± 0.11	1.301 ± 0.025	7.99 ± 0.89	1.32 ± 0.02
		40	5.67 ± 0.06	210.75 ± 13.33	23.51 ± 0.93	0.53 ± 0.09	0.406 ± 0.058	4.485 ± 0.21	1.87 ± 0.27
		80	6.49 ± 0.12	302.50 ± 17.08	41.41 ± 2.03	0.33 ± 0.05	0.332 ± 0.023	3.16 ± 0.25	2.57 ± 0.05
	SCH550	20	5.35 ± 0.01	140.50 ± 7.55	20.81 ± 1.77	0.94 ± 0.05	0.771 ± 0.429	2.33 ± 0.08	1.40 ± 0.13
		40	6.30 ± 0.15	257.50 ± 2.08	22.02 ± 0.47	0.33 ± 0.02	0.209 ± 0.045	0.56 ± 0.31	1.85 ± 0.13
		80	7.20 ± 0.16	345.00 ± 19.24	37.06 ± 1.03	0.25 ± 0.02	0.168 ± 0.028	0.43 ± 0.27	1.87 ± 0.11
	SCP350	20	5.22 ± 0.04	162.00 ± 4.97	22.91 ± 0.91	0.79 ± 0.08	0.682 ± 0.302	5.64 ± 0.18	1.74 ± 0.09
		40	5.89 ± 0.01	316.50 ± 3.87	25.04 ± 0.62	0.50 ± 0.01	0.251 ± 0.023	0.56 ± 0.45	2.09 ± 0.12
		80	6.73 ± 0.01	321.25 ± 4.79	44.71 ± 2.05	0.25 ± 0.01	0.205 ± 0.035	1.45 ± 0.56	3.53 ± 0.08
	SCP550	20	5.69 ± 0.04	200.00 ± 12.33	22.30 ± 0.54	0.36 ± 0.05	0.363 ± 0.089	1.08 ± 0.19	1.34 ± 0.05
		40	6.67 ± 0.05	342.50 ± 77.31	24.90 ± 0.92	0.16 ± 0.01	0.122 ± 0.025	1.31 ± 0.35	1.59 ± 0.03
		80	7.94 ± 0.01	403.00 ± 14.31	47.04 ± 2.06	0.18 ± 0.02	0.119 ± 0.048	0.41 ± 0.89	1.89 ± 0.13
60	S0	0	4.86 ± 0.01	79.00 ± 2.83	21.10 ± 2.30	3.19 ± 0.05	3.044 ± 0.132	12.01 ± 0.40	1.27 ± 0.21
	SCH350	20	5.32 ± 0.04	151.00 ± 10.68	28.80 ± 0.84	0.72 ± 0.05	0.022 ± 0.0004	2.32 ± 0.23	2.76 ± 0.04
		40	5.56 ± 0.23	259.25 ± 5.32	30.62 ± 2.83	0.31 ± 0.03	0.021 ± 0.0008	0.75 ± 0.09	1.96 ± 0.08
		80	7.28 ± 0.31	595.50 ± 16.99	34.59 ± 2.09	0.08 ± 0.02	0.020 ± 0.0005	0.29 ± 0.01	1.96 ± 0.14
	SCH550	20	5.61 ± 0.04	181.00 ± 10.42	28.26 ± 1.45	0.39 ± 0.01	0.022 ± 0.0003	0.63 ± 0.09	2.29 ± 0.08
		40	6.16 ± 0.08	316.75 ± 8.96	28.93 ± 1.92	0.12 ± 0.01	0.021 ± 0.0002	0.17 ± 0.01	2.20 ± 0.47
		80	7.51 ± 0.08	629.75 ± 11.61	33.17 ± 2.05	0.04 ± 0.01	0.020 ± 0.0001	0.29 ± 0.01	2.24 ± 0.01
	SCP350	20	5.54 ± 0.07	204.25 ± 2.97	29.85 ± 1.31	0.46 ± 0.05	0.021 ± 0.001	1.36 ± 0.38	2.61 ± 0.05
		40	6.03 ± 0.02	364.00 ± 15.38	30.59 ± 1.24	0.23 ± 0.03	0.021 ± 0.0003	0.43 ± 0.06	2.82 ± 0.04
		80	7.09 ± 0.10	642.25 ± 17.74	42.19 ± 1.49	0.12 ± 0.01	0.020 ± 0.0001	0.29 ± 0.01	3.73 ± 0.02
	SCP550	20	5.88 ± 0.01	263.00 ± 4.90	29.78 ± 0.44	0.21 ± 0.01	0.021 ± 0.001	0.62 ± 0.30	2.32 ± 0.16
		40	6.70 ± 0.07	496.00 ± 13.44	31.36 ± 1.86	0.06 ± 0.03	0.021 ± 0.0001	0.17 ± 0.06	2.76 ± 0.05
		80	8.15 ± 0.09	871.50 ± 14.61	41.97 ± 2.00	0.04 ± 0.01	0.020 ± 0.0002	0.17 ± 0.01	3.26 ± 0.13

pronounced when amended with CP than CH biochar and for biochar produced at 350°C than when produced at 550°C. An increase in soil organic carbon is because of the presence of recalcitrant carbon (Nyambo et al., 2018) and a decrease in the mineralisation of the soil carbon because of sorption of labile soil organic matter onto the biochar particles (Singh & Cowie, 2014) and/or a very short-term inhibitory effect of microbial activity of biochar-associated volatile organic compounds (Spokas et al., 2011).

3.2 | pH of point of zero charge

The PZC is the pH value for which the net charge because of sorbed ions, other than H^+ and OH^- is equal to zero (Sposito, 2008). Figure 2 shows results of the determination of PZC and it is observed that biochar type amendments to soil increase the pH_{PZC} as compared with the control in the order SCP550 > SCH550 > SCP350 > SCH350. The increment in pH_{PZC} to basic pH values increased with amendment rate for a constant incubation period. The increment in pH_{PZC} after 7 days of incubation for amendment rates 20, 40 and 80 g/kg was in the order 0.44, 0.57 and 1.68 for SCH350, 0.55, 1.02 and 2.01 for SCP350, 0.50, 1.0 and 1.98 for SCH550 and 0.68, 1.76 and 2.32 for SCP550. These same increments was observed for soil–biochar incubated for 60 days with increase in amendment rate in the order 0.78, 0.98 and 2.19 for SCH350, 0.97, 1.55 and 2.32 for SCP350, 0.87, 1.55 and 2.26 for SCH550 and finally 1.09, 1.81 and 2.76 for SCP550. Comparing pH_{PZC} for all types of biochar amendments and same incubation rate, there was a rise in pH_{PZC} from 7 to 60 days of incubation. Research has demonstrated that when pH is higher than the pH_{PZC} of a variable charge soil, the soil possesses a net negative charge on the surface and the potential of the adsorption plane is negative (Xu et al., 2016). In this light, we can estimate that adding biochar to soil considerably varied the surface charges of the soil resulting in the pH_{PZC} greater than the pH_{PZC} of the unamended soil. Thus on moving towards basic pH, one can expect soil–biochar

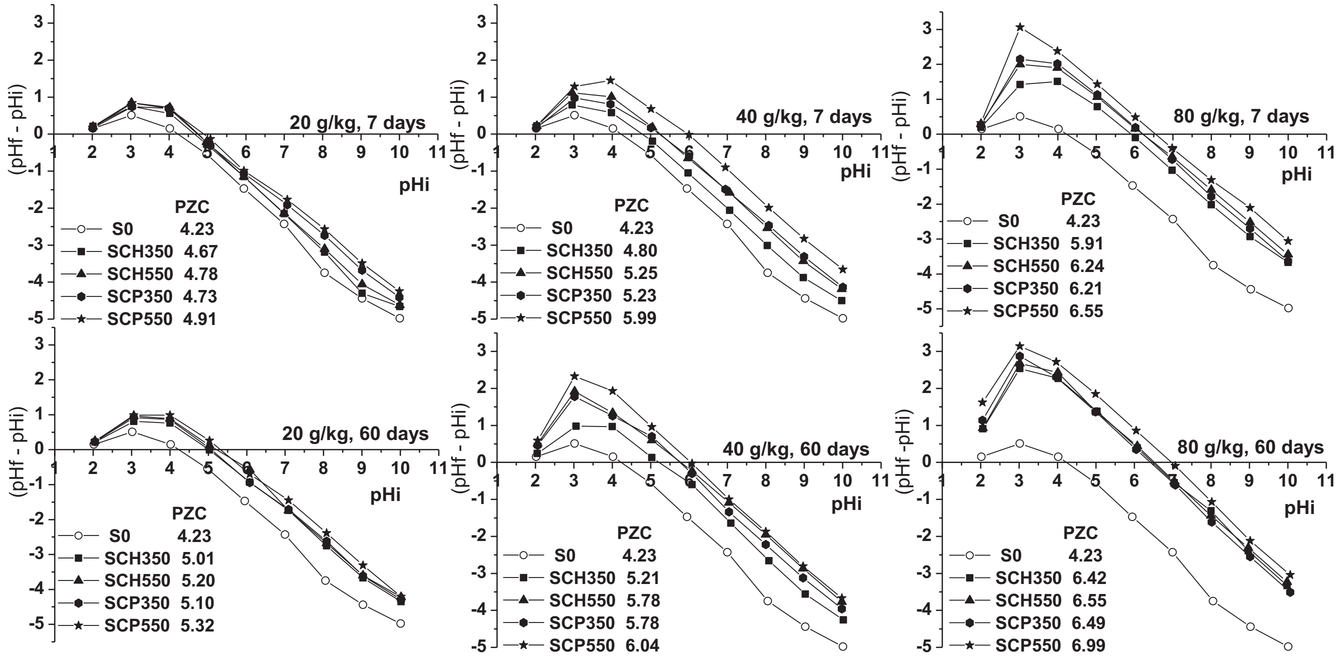

FIGURE 2 Plots of ΔpH vs. pH$_i$ for the determination of point of zero charge for amended soil sample at 20, 40 and 80 g/kg incubated for 60 days.

mixture having a more and more negatively charged surface. This can be attributed to the presence of –COO- and –O- from the biochar and thus may repel negative ions.

3.3 | Phosphorus sorption

This phosphorus sorption study is aimed at determining the amount of P that the soil, soil–biochar adsorb in solution with different concentration of P at equilibrium. The adsorption data fitted in isotherms in other to elucidate the mechanism of adsorption and estimate the adsorption maximum, adsorption capacity and adsorption energies.

3.3.1 | Adsorption of phosphorus on soil

Figure 3 represents the sorption curve for the adsorption of P onto soil incubated for 7 and 60 days. A rapid increase in the adsorption capacities of both soil samples is observed (because of incomplete occupation of adsorption sites), followed by a gradual slowdown for greater concentrations, until the formation of a plateau indicating near saturation of the soil samples is reached. This implies that the vacant adsorption sites for P declines as the concentration of the adsorbate rises (Enang et al., 2019) as the result of strong affinity of the soil to P at small concentrations, which will decrease as concentration rises (Sparks, 2003).

For a more systematic study, the experimental data were interpreted using Langmuir and Freundlich isotherms and the parameters obtained are presented in Table 3. The experimental data of the sorption of P on soil samples fits into the two models ($R^2 > 0.9$) suggesting that the P adsorption is controlled by both Langmuir and Freundlich adsorption mechanisms. This result indicated that the P adsorption could be governed by multiple mechanisms. Adsorption of P on Cameroonian acid soil had let to different conclusion as to the best fit isotherms. Previous work on the fixation of P on soil of the Eastern flank of Mount Cameroon displayed a best fit with a Freundlich model even though both isotherms had a coefficient of determination greater than 0.9 (Mbene et al., 2017). Comparing the P sorption maximum obtained from a Langmuir isotherm of the unamended soil (i.e. amendment at 0 g/kg of biochar), incubated for 7 and 60 days, indicated a slight increase in $Q_{\max}$ and a decline K_L of P with increase in incubation days after wetting the soil samples. We can suggest that, when dry soils are rewet, P mineralisation occurs causing P more available to the soil solution (Laboski & Lamb, 2003), thus resulting in a rise in $Q_{\max}$. Moreover, the P sorption maximum values were more than those obtained from experimental data, indicating that adsorption sites were not all occupied by P with similar results obtain by Njoyim et al. (2016). Also, a decline in binding energy is observed which may indicate a weak attachment of P on the soil surface of S0 after 60 days of incubation. From the Freundlich isotherm parameters, the adsorption capacities and sorption intensity were quite similar. A slight increase in sorption intensity with the soil sample with increasing number of incubation days (0.2570 for S0, 7 days and 0.2671 for S0, 60 days) may tend to prove that S0 at 60 days of incubation have a greater affinity to P adsorption.

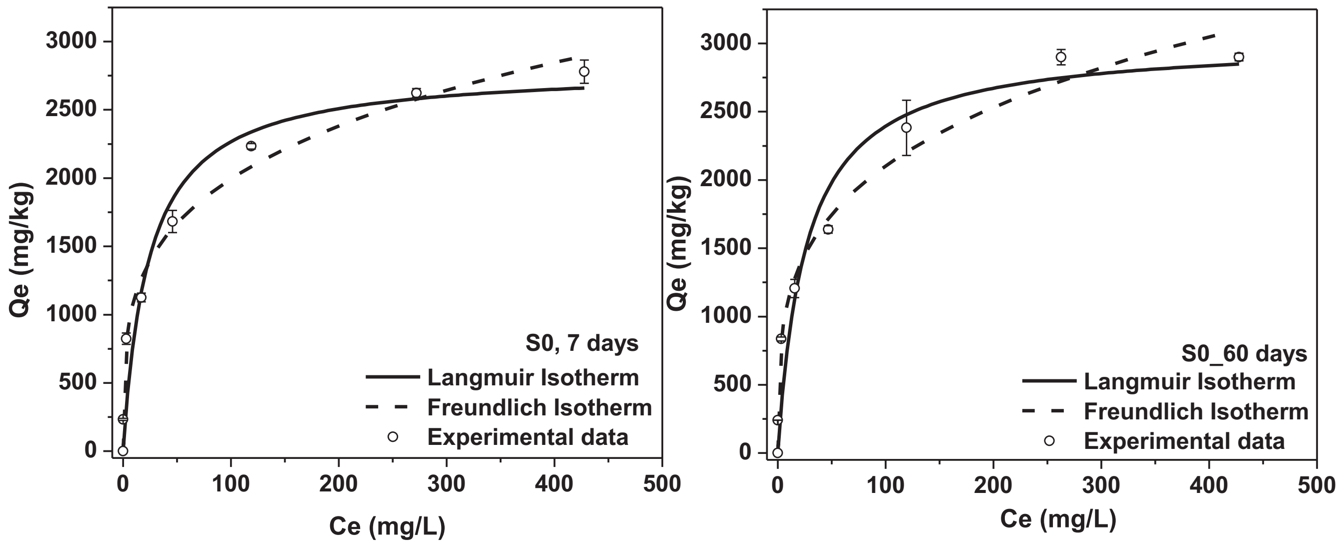

FIGURE 3 Langmuir and Freundlich phosphorus sorption isotherms of soil samples incubated for 7 and 60 days.

TABLE 3 Langmuir and Freundlich parameters for unamended soil (S0).

Material	Incubation days	Langmuir			Freundlich		
		K_L (L/kg)	Qmax (mg/kg)	R^2	$\frac{1}{n}$	K_F (mg/kg)	R^2
S0	7	0.0418	2808.97	0.921	0.2570	610.15	0.986
S0	60	0.0359	3047.82	0.918	0.2671	613.33	0.979

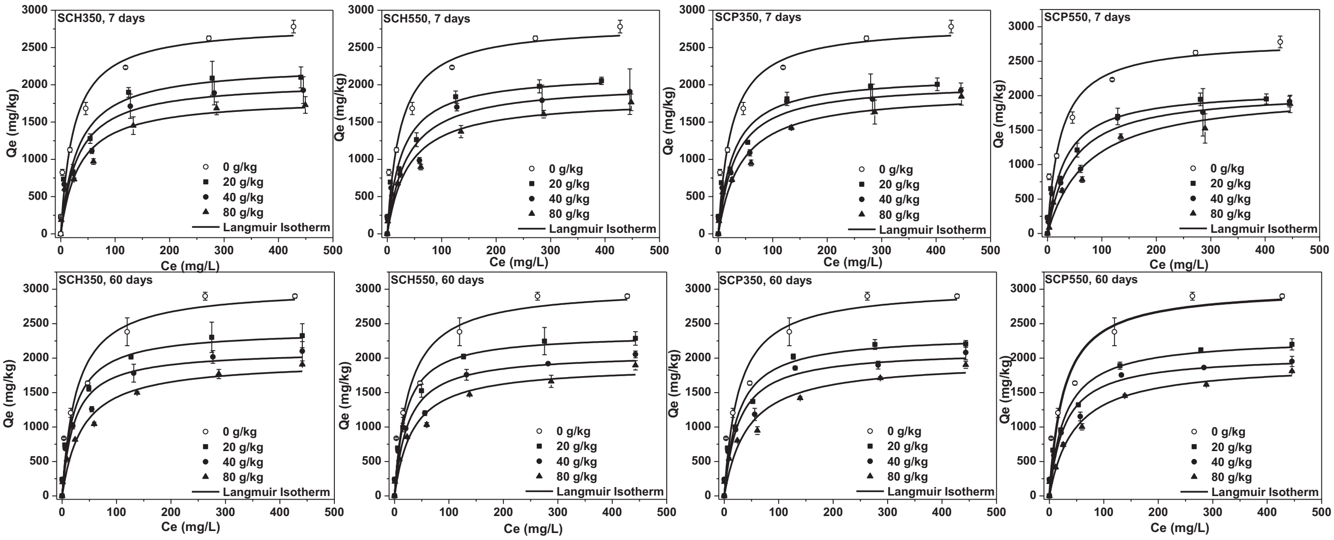

FIGURE 4 Langmuir phosphorus sorption isotherms for SCH350, SCH550, SCP350 and SCP550 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days.

3.3.2 | Adsorption of phosphorus on soil–biochar

Langmuir isotherm model

Figure 4 represents the graph with experimental data fitted to Langmuir curves for the adsorption of P onto soil amended with biochar produced from CH and CP at 350 °C and 550 °C incubated for 7 and 60 days at room temperature. Typical isotherms profile curves and plotted data were observed as in other works (Chintala, Schumacher, et al., 2014; Xu et al., 2014). From Figure 4, we can observe that the plateaus of the amended soil samples were below the control for all four biochar additions and irrespective of the incubation periods. This indicates that the adsorption capacities and activity of the adsorption sites were reduced. A logical explanation can be that P released from biochar was sorbed to the soil surface and filled sorption sites, some of which are reversible (Sato & Comerford, 2006). This situation leaves fewer available P sorption sites, reducing the total capacity for the sorption of P from external sources. Thus this study illustrates that biochar can reduce the soil's P-fixing potential. From Figure 4, we observed that, the level of the plateau for all the four biochar declines with increase amendment rate from 20 to 80 g/kg, thus indicating a reduction in adsorption capacities with increase amendment rate. From the Langmuir isotherm parameters, P sorption maximum declines with increasing amendment rate for all four biochar types. For example, Q_{max} are 2267, 2048 and 1823 mg/kg for amendments with CH350 and 2122, 20,322 and 1904 mg/kg for amendments with CP350 at amendment rates of 20, 40 and 80 g/kg for 7 days respectively. Studies have shown that adding biochar reduces the sorption maximum of P (Eduah et al., 2019), but at greater biochar amendment rates the sorption maximum is more than the unamended soil (Xu et al., 2014). From these observations, it appears that the amendment rate of the biochar in this study was not sufficient to let the soil–biochar mixture to adsorb P more than the control. It was observed that, when the biochar rate increases, the pH of the soil–biochar mixture rises (Table 2), which affects the adsorption of P (Haynes, 1982) because of the formation of more negative charges on the surface of the soil–biochar samples as confirmed by the PZC analysis, thus increasing repulsion of anionic P forms (Chintala, Schumacher, et al., 2014; Murphy & Stevens, 2010). It is observed that, soil amended with biochar produced at higher temperature had a reduced P sorption maximum for all four biochars. The EC of amended soil was found to increase with biochar produced at higher temperature (Table 2) which will increase the ionic strength of solution and may reduce the positive electric potential of the soil surface through a screening effect and ultimately reduce the P sorption (Chintala, Schumacher, et al., 2014). At amendment rates of 20, 40 and 80 g/kg after 7 days of incubation, Q_{max} for SCH350 were 2267, 2048 and 1823 mg/kg which increased to 2407, 2112 and 1990 mg/kg after 60 days of incubation. This tendency was observed for all four biochar additions with respect to increased incubation days. In general, it was observed that soil–biochar with CP biochar had a lesser P sorption maximum as compared with those incubated with CH biochar for 7 days of incubation, whereas, at 60 days of incubation the adsorption maximum were more or less the same. Other studies, however, showed reduction in phosphate sorption in

TABLE 4 Langmuir and Freundlich parameters for soil–biochar samples incubated for 7 and 60 days.

		7 days						60 days					
		Langmuir			Freundlich			Langmuir			Freundlich		
Material	Amendment rate	K_L(L/kg)	Q_{max}(mg/kg)	R^2	$\frac{1}{n}$	K_F (mg/kg)	R^2	K_L (Lk/g)	Q_{max} (mg/kg)	R^2	$\frac{1}{n}$	K_F (mg/kg)	R^2
SCH350	20	0.0321	2266.50	0.900	0.2624	459.26	0.945	0.0462	2406.70	0.953	0.2541	535.34	0.965
	40	0.0321	2047.84	0.914	0.2777	381.56	0.952	0.0456	2112.20	0.930	0.2587	459.87	0.979
	80	0.2932	1822.81	0.920	0.2966	302.35	0.961	0.0259	1989.76	0.960	0.3181	287.53	0.984
SCH550	20	0.0369	2158.46	0.924	0.2659	442.10	0.966	0.0497	2354.38	0.968	0.2554	522.89	0.961
	40	0.0278	2024.98	0.911	0.2987	328.55	0.938	0.0410	2070.32	0.938	0.2680	421.94	0.974
	80	0.0256	1815.06	0.936	0.3236	254.09	0.981	0.0303	1891.18	0.945	0.3039	303.71	0.984
SCP350	20	0.0367	2128.84	0.919	0.2659	434.68	0.966	0.0398	2336.48	0.947	0.2640	483.25	0.951
	40	0.0320	2031.83	0.932	0.2897	353.65	0.927	0.0382	2116.30	0.933	0.2718	417.63	0.955
	80	0.0239	1903.78	0.937	0.3255	260.56	0.979	0.0233	1960.86	0.927	0.3215	273.90	0.991
SCP550	20	0.0318	2100.26	0.927	0.2775	394.31	0.969	0.0352	2295.46	0.952	0.2764	436.19	0.970
	40	0.0225	2069.86	0.927	0.3287	274.20	0.931	0.0353	2043.31	0.954	0.2793	381.66	0.952
	80	0.0134	2069.43	0.952	0.4089	157.72	0.954	0.0217	1927.41	0.974	0.3301	251.66	0.969

acidic soils as a result of biochar application because of precipitation of Al^{3+} and Fe^{3+} (sites for phosphate complexation) (DeLuca et al., 2015) and increase in repulsion by the negative charges newly created in the soil, by $-O^-$ and $-COO^-$ from biochar (Martínez et al., 2017). This can be confirmed with the rise in soil organic carbon content (Table 2). In this study, we observe that biochar added to soils serves as a source of P rather than as a sink, resulting in greater availability of P to soils with increasing biochar rate.

Binding energy data (Table 4) obtained from Langmuir isotherms showed a decline with increasing amendment rate irrespective of biochar type and number of incubation days. For example, soil amended with CH550 for 60 days of incubation had a drop in binding energy from 0.0497, 0.0410 and 0.0303 L/kg and for SCP550 after 7 days of incubation; the drop was from 0.0318 to 0.0225 then 0.0134 L/kg for amendment rates of 20, 40 and 80 g/kg respectively. Also, the binding energy increase in the soil–biochar mixture amended with biochar produced at lower temperature, that is, in the order SCH350 > SCH550 and for SCP350 > SCP550. Also, binding energy increased with increasing number of incubation days for each biochar type and corresponding amendment rate. For example, the increase in binding energy from 7 to 60 days for the soil–biochar mixture amended with 20 g/kg of CH550, was 0.0369 to 0.0497 L/kg, 0.0278 to 0.0410 for 40 L/kg and then from 0.0256 to 0.0303 L/kg for 80 g/kg and the case of SCP550 the binding energy was 0.0318 to 0.0352 L/kg, 0.0225 to 0.0353 for 40 g/kg and then from 0.0134 to 0.0217 L/kg for 80 g/kg. The order of decreasing binding energy of soil–biochar samples suggests that P can be easily desorbed. These results suggest that, compared with active sites in the original acidic soil, newly developed hydr(oxide) in the biochar-amended soil might retain phosphate ions more loosely (Baninajarian & Shirvani, 2020; Xu et al., 2014). Increased amendment rates in soil–biochar mixtures results in an increase in pH, reduced concentrations of free Fe, Al and Mn oxides which may be transformed to Fe, Al and Mn hydroxides and reduced the availability of high energy sorption sites (Stevenson & Vance, 1989). Generally, phosphates are strongly fixed to acidic soils not only through chemisorption on high-energy surfaces of Fe and Al oxides and hydroxides but also via precipitation of Al and Fe phosphate. However free Al and Fe concentrations in biochar-amended soil are lessened (Table 2) thereby reducing the availability of high energy sorption sites for phosphate ions (Dume, Tessema, et al., 2017).

In general, it was observed that soil–biochar mixtures with CP had a smaller P sorption maximum as compared with those incubated with CH after 7 days of incubation, whereas, at 60 days of incubation the adsorption maximum were more or less the same. For all biochar, the P sorption maximum obtain from a Langmuir isotherm model were greater than from experimental data indicating that all the biochar sites were not occupied by P.

Freundlich isotherm model

Figure 5 represents simulated Freundlich curves for the adsorption of P onto soil amended with biochar produced from CH and CP at 350°C and 550°C incubated for 7 and 60 days at room temperature. This simulated curve profile, is similar to the Freundlich curve for S0. From Table 4, it is observed that the sorption capacities (K_F) of soil–biochar mixtures are less than the control (S0), which can be

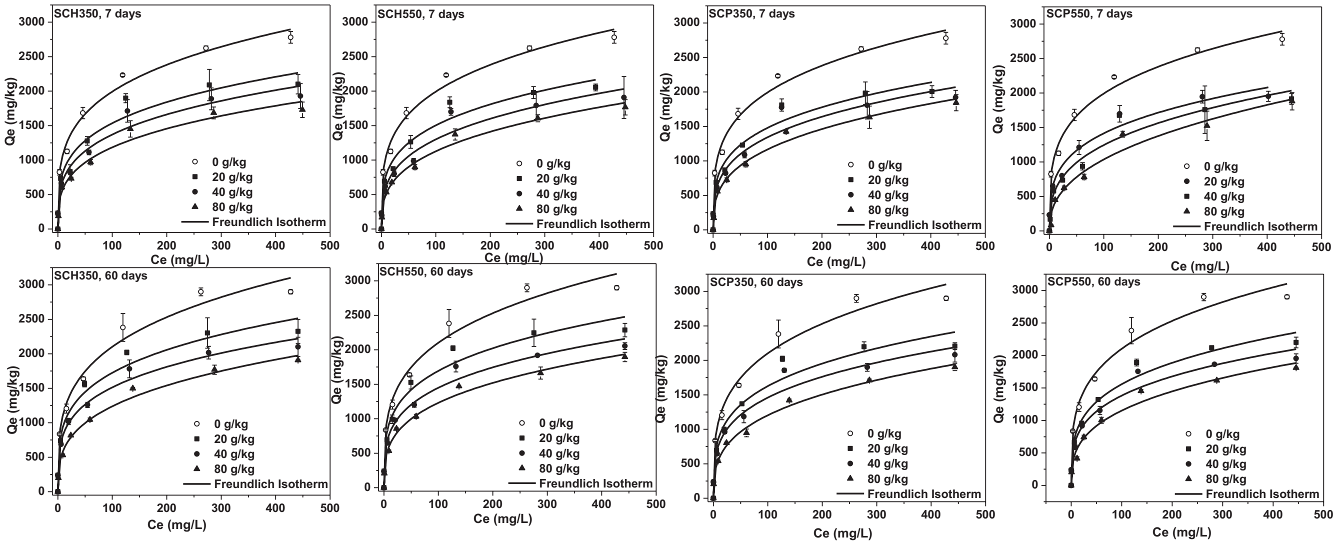

FIGURE 5 Freundlich phosphorus sorption isotherms for SCH350, SCH550, SCP350 and SCP550 at amendment rate of 0, 20, 40 and 80 g/kg incubated for 7 and 60 days.

related to the lesser P sorption maximum for soil–biochar mixtures. Also, a decline in sorption capacity with increasing incubation rate for all the biochar types, irrespective of incubation period, was observed. As an example, at 60 days of incubation, soil amended with CH350 showed a decrease in sorption capacity from 535, 460 to 286 mg/kg and with CP350 amendment, the decrease was from 483, 418 to 274 mg/kg with increases in amendment rate of 20, 40 and 80 g/kg respectively. Soil amended with biochar pyrolysed at higher temperature, had a significant decrease in P sorption capacity. Moreover it was noted that increase in incubation days from 7 to 60 days increases P sorption capacity of the soil–biochar samples for all biochar types. For example, comparing the rise in sorption capacity between 7 days and 60 days of incubation for SCH350 was 459 to 535 for 20 g/kg, 382 to 459 for 40 g/kg and 302 to 288 for 80 g/kg. The sorption intensity $\frac{1}{n}$ is used to describe the heterogeneity of the adsorption surface. The affinity of P adsorption on soil–biochar increases as $\frac{1}{n} \approx 1$. From Table 5, the sorption intensity of SCH350, SCH550, SCP350 and SCP550 is slightly greater than for S0 after 7 days of incubation, while for 60 days of incubation, the sorption intensity of SCH350, SCH550, SCP350 and SCP550 at rate of 20 and 40 g/kg presents a relatively smaller or the same sorption intensity with S0, but with amendment rate of 80 g/kg, the sorption intensity was greater, while for CP350 and CP550 soil amendments, the sorption intensity were greater than for S0 for all amendment rates. Increasing the number of incubation days; decreases the sorption intensity of P onto the soil–biochar mixture. Thus for greater $\frac{1}{n}$ values, the adsorption of phosphate to soil–biochar mixture was favourable and happened on heterogeneous surfaces. Previous studies were consistent with this observation as reported by Yao et al. (2011), who indicated a low adsorption capacity with biochar derived from sugar beet tailing same as Xu et al. (2014) incubated acidic soil samples with wheat straw biochar. The decrease in sorption capacity of the soil–biochar mixture which is closely related with sorption maximum from Langmuir data can be due to variation in physicochemical properties of the samples. An increase in pH and PZC of the samples, will lead to increase in negative charge surfaces, thereby increasing repulsion, thereby reducing P sorption capacity (Murphy & Stevens, 2010). Higher pH depresses the formation of HPO_4^{2-}, which is preferentially adsorbed by soil colloids (Xu et al., 2014).

3.4 | Phosphorus desorption from soil and soil–biochar mixture

The extent of desorption of P from these samples can indicate the degree of P availability in the soil solution and to plants. In this work, the P desorption percentage was used to evaluate the quantity of P desorbed from soil and soil–biochar mixtures as presented in Table 5. Results showed that, the amount and percentage of P desorbed were influenced by biochar type, biochar production, the rate of amendment and the number of incubation days. P desorption from biochar amended soils were greater than unamended soil. This is because of the fact that during amendment of soil with biochar, P is released from biochar and sorbed onto strong adsorption sites which is not reversible (Sato & Comerford, 2006). This process leaves fewer adsorption sites for P, therefore newly sorbed P will be on low energy adsorption sites, which may ease desorption. Also, the presence of acid-functional groups such

TABLE 5 Percentage desorption of P from soil and soil–biochar mixture.

		7 days			60 days		
Material	**Amendment rate**	P_{sorbed}	$P_{desorbed}$	DP (%)	P_{sorbed}	$P_{desorbed}$	DP (%)
S0	0	1571.19	429.00	27.30	1516.16	412.45	27.20
	20	1223.21	384.62	31.44	1299.33	376.69	29.00
SCH350	40	1164.72	392.05	33.66	1113.33	368.32	32.63
	80	1017.58	412.37	40.52	894.49	346.67	38.76
	20	1213.08	452.01	37.26	1216.33	375.85	30.90
SCH550	40	1146.62	389.28	33.95	1076.17	360.69	33.52
	80	846.79	394.52	46.59	944.18	372.41	39.44
	20	1205.46	392.95	32.60	1186.92	373.25	31.45
SCP350	40	1137.60	375.57	33.01	1058.28	366.95	34.67
	80	882.53	386.37	43.78	890.86	361.73	40.60
	20	1161.99	381.29	32.81	1205.12	365.76	30.35
SCP550	40	1052.36	360.35	34.24	1013.20	385.49	38.05
	80	858.76	364.95	42.50	820.84	332.06	40.45

as carboxylic and phenolic groups on the biochar causes P removal from clay minerals through ligand exchange and or enhanced ligand dissociation of oxides and hydroxides of Fe and Al (Kirk et al., 1999). Cocoa pod biochar amended soil had a greater P desorption percentage than CH biochar amended soil samples. Soil–biochar mixtures with high temperature pyrolysis biochar desorbed P more than the low pyrolysis temperature biochar at amendment rates of 40 g/kg and 80 g/kg. Whereas at 20 g/kg, there was no significant change in P desorption. It was observed that higher pyrolysis temperature biochar adsorbed less than low pyrolysis temperature biochar for the same amendment rate, but desorbs more. Increase in amendment rate, elevate the desorption percentage of P from the soil–biochar mixtures. The desorption percentage increased by more about 10% for all biochar types from 20 mg/kg to 80 mg/kg amendment rate. An increase in incubation days for soil–biochar mixtures resulted in a decline in desorption percentage of P. In all cases, an increasing P desorption percentage, was related to a decline in binding energy for soil–biochar samples as can be seen in Table 5. Previous research corroborated the assertion that a decrease in binding energy increased desorption of P which was attributed to increase in soil pH with biochar application (Eduah et al., 2019).

4 | CONCLUSION

This work demonstrates that acid soil amended with biochar produced at different pyrolysis temperatures influenced the soil chemical properties dissimilarly and decreased soil P sorption capacity as compared with the control. The incubation study of acid soil revealed an increase in soil pH and electrical conductivity with application of biochar at different incubation rates. A marked reduction in exchangeable acidity, Al and Fe occurred after incubation. Thus biochar shows a potential for mitigating soil acidity. Furthermore, phosphate sorption by these amended soils was satisfactorily described by Langmuir and Freundlich models. A reduction in P sorption capacity was observed as compared with the control. The desorption process of P from soil–biochar mixtures was enhanced at greater biochar rates and pyrolysis temperature. From this study we can suggest that P retention and availability can be modulated when biochars are applied at a convenient rate and pyrolysed at an appropriate temperature of about 550 °C. Thus, biochar can be appropriate for P management practices for acid soils in the Western region of Cameroon. Field study with locally produced biochar should be directly applied to farm lands in other to evaluate the fate of applied phosphate fertilizers.

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CONFLICT OF INTEREST STATEMENT

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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