

Research Article

Phosphorus Adsorption and Its Correlation with Physicochemical Properties of Volcanic-Influenced Soils of Meupi-Awing in Northwest Cameroon

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This study evaluated the physicochemical properties and phosphorus adsorption characteristics of surface soils (0–30 cm) of Meupi on the flank of Mount Lefo-Awing. In volcanic-influenced soils, usually characterized by high acidity, phosphorus is often not readily available to plants, and this deficit tends to limit plant growth. Soil physicochemical properties and phosphorus adsorption studies were carried out using standard techniques. Results of soil physicochemical studies showed that the soils were strongly acidic (pH ranged from 4.7 to 5.1), with low available phosphorus (5.47 to 6.97 mg/kg). The apparent equilibrium time for phosphorus to be adsorbed in the analyzed soils was 24 hours. Phosphorus sorption studies revealed that the rate of phosphorus adsorption increased with an increase in the concentration of added phosphorus but decreased at a certain level at higher concentrations because the soil had no more capacity to adsorb phosphorus. The degree of fitness (R^2) of the phosphorus adsorption data for the different adsorption models was in the order Langmuir < Temkin < Van Huay < Freundlich. This suggested that the Freundlich isotherm model was the best fit to describe P sorption processes in soils. The pseudo-second-order kinetics model, which assumed that the rate of phosphorus sorption was dependent on the number of active sites, gave a good fit to predict and describe the kinetics of phosphorus sorption from the soil solution. The capacity of the soil to adsorb phosphorus significantly correlated positively with amorphous Fe ($r=0.953$ and $p < 0.05$), free Fe ($r=0.984$, 0.976 and $p < 0.05$), free Al ($r=0.994$ and $p < 0.01$, $r=0.988$ and $p < 0.05$), and clay ($r=0.968$ and $p < 0.05$), which were the main parameters considered as predictors of phosphorus adsorption activities in the soils.

1. Introduction

Agriculture in recent years has been a challenge to farmers due to the fixation of some most important nutrients of soil. Physicochemical properties of soils are important factors that determine the yield of crop production [1,2]. Soil is a major source of nutrients needed by plants for growth and development [3]. Amongst the three primary plant nutrients, nitrogen (N), phosphorus (P), and potassium (K), which constitute the NPK fertilizer, N and K are readily

available to plants, whereas P is most times unavailable to plants. This unavailability of P in plants makes it the most limiting nutrient in the soil [4], and this deficiency reduces plant growth and development and as such limits crop yield. The main reason for the limited bioavailability of soil P is its high immobilization (sorption and precipitation) rate and its slow release into the soil solution [1,5]. Although P concentration might be high in soils, most of this P is in an unavailable form to plants [6]. Soil phosphate exists both in organic and inorganic forms. The inorganic form is

predominant in the soil and exists as orthophosphates in soil solution for plant uptake [7].

Phosphorus is also involved in an array of processes in plants such as photosynthesis, respiration, nitrogen fixation, flowering, fruiting, and maturation [7–9]. Phosphorus is necessary for early plant growth and development because of the need for rapid cell division [10,11]. Plants may absorb P either as primary monobasic phosphate (H_2PO_4^-) ions or small amounts of the secondary dibasic phosphate (HPO_4^{2-}) ions and the phosphate (PO_4^{3-}) ions [12,13]. Phosphorus has poor solubility, and phosphorus fertilizers suffer from low availability of soluble phosphorus for plant uptake. Phosphorus is highly immobile due to soil interactions such as adsorption and precipitation, as well as the transformation into the organic form. Additionally, excessive phosphorus fertilization significantly enlarges the risk of phosphorus loss through leaching, runoff, and erosion.

As plants remove P from the soil solution, P is replenished by the active pool, and the rate of replenishment depends on the soil pH. Soil solution P is replenished by (i) desorption of sorbed P from soil minerals, (ii) the activity of soil organisms on soil organic matter to release P that was complexed with the positively charged soil organic matter, and (iii) the application of fertilizer and organic amendments to the soil. Recently, more attention has been paid to the biochar-based slow release of fertilizers (SRFs) due to the unique properties of biochar. Researches reveal the beneficial role of biochar in soil amendment. The unique properties of biochar provide a platform for loading nutrients to improve fertilizer efficiency. Conventional chemical fertilizers suffer from the drawbacks of rapid nutrient leaching, serious environmental pollution, and significant economic burden, and biochar-based slow release of fertilizers receives increasing global attention [13]. Most soils in the tropics, with Cameroon inclusive, suffer from a limited supply of P due to the presence of oxides and hydroxides of iron and aluminium in these soils that fix the soluble P, and this process is accelerated by low soil pH. At low pH values, the oxides and hydroxides of Al and Fe are highly soluble and react with phosphate ions (H_2PO_4^-) to form hydroxyl phosphate that is insoluble and unavailable for plants [1,14].

Many farmers in Cameroon use phosphorus fertilizers to improve their agricultural yields, and it is thus necessary to determine the rate at which soils adsorb P [15]. Volcanic-influenced soils are known for higher levels of P fixation due to their acidic nature. Little knowledge is available about the relationship between the phosphorus fixing capacity of soils from Meupi on the flank of Mount Lefo in Awing-Santa and soil physicochemical properties. Volcanic ash soils, by virtue of the short-range order variable charged nanomaterials (allophane, imogolite, Al and Fe oxides, and organic mineral complexes), may adsorb high amounts of phosphate characterized by high surface area and reactivity [16].

The sorption isotherm is a functional relationship quantifying the adsorbed amount as a function of the solution concentration in dynamic equilibrium [17]. It is intensively used to describe the behavior of P in a wide range of soils and environmental conditions; estimate P concentration in the aqueous phase of soil, the amount of

P adsorbed by the soil, and energy of P adsorbed; and identify the properties of the soil that are responsible for P adsorption in acidic soils [18]. Empirical as well as more thermodynamic-based equations, including Freundlich and Langmuir models, are commonly used to describe the sorption behavior of phosphate in soils [19].

The general objective of this study was to evaluate the P adsorption capacity of soils of Meupi and its effects on the physicochemical properties of the soil. The specific objectives were to determine the physicochemical properties of surface soil (0–30 cm) samples selected from Meupi and then study their P adsorption capacity using Langmuir, Freundlich, Temkin, and Van Huay isotherm equations and finally investigate the relationships between P adsorbed by the soil and some relevant soil physicochemical properties.

2. Materials and Methods

2.1. Sites Descriptions. Awing is located in the grass field zone of Cameroon, precisely in the Santa Subdivision of the Northwest Region of Cameroon. It is situated at about 21 km southeast of Bamenda town. Awing has a surface area of about 480 km², and as of the year 2010, its population density stood at 115.2 people/km. Located between latitudes 05°47' and 06°00' north of the equator and longitudes 10°10' and 10°22' east of the Greenwich Meridian, Awing has an elevation of about 1,206 m above sea level. Its topography is trough-like, low-lying plain, surrounded by an extension of the volcanic chain of the Bambouto Mountains in the west, north, and east, hemmed by a network of hills. The highest point here is Mount Lefo (the fourth highest mountain in Cameroon), with a height of 2,550 m on whose northern flank is Lake Awing. The annual maximum temperature varies between 27.2°C and 33.6°C, whereas the annual minimal temperature varies between 7.8°C and 15.9°C. Pluviometry varies between 1,270 mm and 1,778 mm of water per year. Its hydrology is characterized by the existence of small rivers, streams, springs, and swamps. The soils from this area show andic properties, with an accumulation of free and amorphous oxides and hydroxides of iron and aluminium [20,21].

Sampling was done in February 2021 along the flank of Mount Lefo-Awing. The study site has two distinct climates, rainy and dry seasons. Two sampling sites (Meupi West and Meupi East) were chosen for sample collection, and in each site, a random sampling technique was used. Two surface soil samples (0–30 cm) were collected from each of the sampling sites (one from cultivated farmland and another from virgin land). Meupi East is located at longitude 10°13'20"E and latitude 05°50'6.0"N, with an elevation of 1,436 m above sea level (handheld Global Positioning System (GPS) Garmin eTrex Vista C). Two soil samples with codes: Meupi East Cultivated (MEC) and Meupi East Virgin (MEV), were collected from Meupi East. Meupi West (MW) is located at longitude 10°13'22"E and latitude 05°50'0.2"N, with an elevation of 1,426 m above sea level. Two soil samples: Meupi West Cultivated (MWC) and Meupi West Virgin (MWV), were collected from this site.

2.2. Laboratory Analysis. Newly collected soil samples were air-dried in the laboratory, powdered in a porcelain mortar using a pestle, and sifted through a 2 mm sifter. The prepared soil samples were thereafter analyzed for various physico-chemical properties using international standard methods [22–24] prior to P sorption studies. All reagents used in this study were of analytical reagent grade.

2.3. Physicochemical Analysis. Soil pH was measured over a 1:2.5 soil:solution ratio in 1 N KCl (pH-KCl) and distilled water (pH-H₂O) with the help of a pH meter. The electrical conductivity (EC) was measured over a 1:5 soil-water solution ratio with a conductometer (MTW MODEL). Organic carbon (OC) was determined by the oxidation of OC by potassium dichromate (K₂Cr₂O₇) in the presence of concentrated sulfuric acid followed by titration with hydrated iron (II) sulfate (FeSO₄·7H₂O) [25], and organic matter (OM) was calculated from the levels of organic carbon in the soil by multiplying by 1.72 as reported by Hazelton and Murphy (2007) [26]. Exchangeable bases were determined following the Schollenberger method using a 1 M ammonium acetate solution buffered at pH 7, and after which, the amount of Na⁺ and K⁺ ions in the extract were determined by flame photometry. The amount of Ca²⁺ and Mg²⁺ ions were determined by complexometric titration. Cation exchange capacity (CEC) was determined as a direct continuation of the Schollenberger method using a 1 N KCl solution for the displacement of ammonium ions, and the desorbed ammonium ions were determined by the Kjeldahl's distillation method using 0.02 N HCl and 0.02 N NaOH solutions. Exchangeable acidity was determined according to the procedures outlined by [23], in which 1 M KCl solution was added to the soil sample, agitated, and filtered, and the concentrations of cations (Al³⁺ + H⁺) were determined by titration against standard 0.02 N NaOH solution using phenolphthalein indicator. Total nitrogen (% N) was determined by completely mineralizing the total N in the soil with a mixture of concentrated H₂SO₄ solution and salicylic acid at 80°C in the presence of a catalyst (mixture of 100 g K₂SO₄ + 20 g CuSO₄ + 2 g selenium). The mineralized extract was distilled with an excess 0.01 N NaOH and titrated with 0.01 N H₂SO₄ (Kjeldahl's distillation method). Free Fe and Al were determined colorimetrically after their reduction with dithionate citrate bicarbonate (DCB), whereas amorphous Fe and Al were determined colorimetrically after their reduction with ammonium oxalate in the dark. Available P was determined by Bray 2 method. Particle size (texture) was determined by the hydrometer method.

2.3.1. Phosphorus Adsorption Studies. The equilibrium time of P adsorption in the soil was first determined, and then the P adsorption studies were performed using the equilibrium time, and finally, the kinetics of P adsorption from soil solution was done. Phosphorus adsorption studies were carried out following the methods described by [27,28].

Determination of equilibrium time. Phosphorus solutions of 0, 10, 50, 100, and 250 ppm P were prepared using distilled

water from a mother solution of ammonium dihydrogenophosphate (NH₄H₂PO₄) containing 1,000 ppm P solution using the dilution formula. Twenty-five subsamples were formed from Meupi West Virgin (MWV) soil by accurately weighing 5 grams of air-dried soil samples into clean 250 mL glass bottles (with 5 subsamples studied at each concentration of P: 0, 10, 50, 100, and 250 ppm, at different time intervals in hours). Fifty milliliter of each P solution was added to them and shaken for 5, 10, 15, 24, and 30 hours at 25°C on an end-to-end shaker (Edmund Buhler SM 25 model) at 125 oscillations per minute. The soil suspension was filtered through a Whatman number 2 filter paper and centrifuged at 3,000 rpm for 30 minutes with a model HRT 20 MM multifunctional intelligent centrifuge to get the clear solution. One milliliter extract of each sample and the blank solution were pipetted into test tubes, and 2.5 mL of a mixture containing ammonium molybdate and sulfuric acid, 2.5 mL of ascorbic acid, and 10 mL of distilled water were then added successively and mixed. The test tubes were then put in a water bath at 85°C for 10 minutes to enhance color development. After the blue color developed, the P concentration was determined colorimetrically at a wavelength of 665 nm [28]. Each soil sample was analyzed in duplicate. The amount of P adsorbed by the soil (X) was calculated by the difference between the quantity of P initially present (C_0) and the quantity of P in solution (C_e) after treatment using the following equation:

$$X = \frac{(C_0 - C_e) * V}{m}, \quad (1)$$

where V = volume (L) of P solution added and m = mass (kg) of soil sample.

The equilibrium time of P adsorption in the soil was taken to be the least time in the range of times for which there was no change in the amount of P adsorbed by the soil.

Using the equilibrium time obtained, the four soil samples (MWC, MWV, MEC, and MEV) were then analyzed for phosphorus adsorption studies. Five grams each of air-dried soil samples were used in this study, and the same procedure as to the equilibrium time for P adsorption analysis was followed. The amount of P adsorbed was calculated using equation (1).

2.4. Kinetics of Phosphorus Adsorption. This study was carried out on the Meupi West Virgin soil sample only. Five grams each of air-dried soil samples were put into nine glass bottles. Two milliliter of potassium phosphate solution (K₃PO₄ stock solution of 20 ppm) was added to each flask, followed by 18 mL of distilled water. All flasks were then stirred at 150 rpm for 24 hours in a GFL 3017 shaker, at 25°C. Equilibration mixtures were removed from the shaker after the following time (hours) intervals (t): 1, 2, 4, 8, 12, 18, 24, 36, and 48 hours for analysis. The amount of P adsorbed was calculated using equation (1). The P adsorption data obtained were analyzed graphically by plotting P adsorbed as a function of time to give a kinetic curve. The adsorption reaction order was determined after the P adsorbed data were linearized into different kinetic models and tested.

The P adsorption data obtained were analyzed graphically by plotting P adsorbed as a function of equilibrium concentration to give nonlinear adsorption isotherms and using the linear isotherms of Freundlich, Langmuir, Temkin, and Van Huay to transform the data into linear equations which were then used to calculate P adsorption coefficients. The linear forms of the various adsorption isotherms are defined as follows.

Freundlich isotherm expresses the variation of an adsorbed quantity with equilibrium concentration. The linear equation is defined as follows:

$$\log X = \frac{1}{n} \log C + \log K_f, \quad (2)$$

where X = amount of phosphorus adsorbed (mg kg^{-1}), n = constant whose value depends on the adsorbent, C = concentration of phosphorus in equilibrium solution (mg L^{-1}), and K_f = adsorption equilibrium constant related to the boundary energy at the surface (mg kg^{-1}).

Langmuir's linear equation for the adsorption of solutes in solution is defined as follows:

$$\frac{C}{X} = \frac{C}{X_m} + \frac{1}{K_L X_m}, \quad (3)$$

where X = amount of phosphorus adsorbed (mg kg^{-1}), X_m = maximum adsorption capacity (amount of adsorbate needed for a monolayer coverage) in mg kg^{-1} , K_L = constant related to the boundary energy of the soil at the surface (L mg^{-1}), and C = concentration of phosphorus in equilibrium solution (mg L^{-1}).

For the Temkin adsorption isotherm, the energy of adsorption is a linear function of the surface coverage. Temkin isotherm equation is defined as follows:

$$X = a + b \ln C, \quad (4)$$

where a = amount of P adsorbed of Temkin model (mg kg^{-1}), b = buffer capacity of Temkin model (mL g^{-1}), X = amount of P adsorbed (mg kg^{-1}), and C = equilibrium solution concentration (mg L^{-1}).

The Van Huay isotherm is defined as follows:

$$\frac{X}{m} = m + n\sqrt{C}, \quad (5)$$

where X = amount of phosphorus adsorbed (mg kg^{-1}), C = concentration in fluid phase (mg L^{-1}), n = Van Huay adsorption coefficient (L kg^{-1}), and m = Van Huay constant parameter.

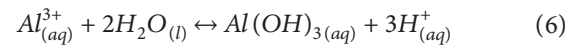
2.4.1. Statistical Analysis. The Student's test (t -test) was used to compare P adsorption between soil samples from different sampling sites (MWC, MWV, MEC, and MEV). ANOVA was used to verify if there was any significant difference between the mean results of P adsorbed. Correlation

analyses were performed between P adsorption data and some important soil physicochemical properties. Statistical analysis was done using the Statistical Package for Social Sciences (SPSS) version 20 and Origin 2018 software.

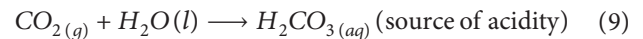
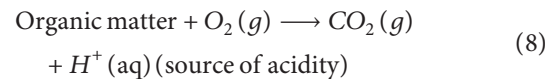
3. Results and Discussion

Physicochemical properties of the soils are presented in Table 1.

The results of physicochemical properties showed that the virgin soils (MEV and MWV) were very strongly acidic with pH water ranging from 4.5 to 5.0, while the cultivated soils (MWC and MEC) were strongly acidic with pH water ranging from 5.1 to 5.5, according to the ratings by [26]. The high acidity of the virgin soils could be due to soluble metal ions of Al and Fe (acidic cations), which react with water releasing H^+ according to the following equations:



The strongly acidic nature of the cultivated soils could probably be due to decaying organic matter (equations (8) and (9)) that produces H^+ , which is responsible for the increase in soil acidity.



The application of ammonium sulfate fertilizer (as indicated by the farmers on-site) to cultivated soils could also be a major cause of the low soil pH [29]. The sign and magnitude of ΔpH , which relates to the sign and magnitude of soil surface charge, were negative for the soils, signifying that these soils were above their point of zero charges. Thus, the soils had net negatively charged surfaces, and hence a net CEC at field pH [3]. Many crops grow best when the soil pH is between 6.0 and 8.2. Thus, the pH results showed that the cultivated soils need liming to raise soil pH to an optimal level needed for crop growth.

According to the ratings established by [26], all soil samples showed low salinity, ranging from 0.01 to 0.03 mS/cm. The low range of EC indicates that tolerant crops and sensitive crops will not be affected if cultivated on these soils. This low EC could be due to the optimum temperature of soils in this area, which led to lower soil-water temperature, and as such, ion movements under electrostatic potential were slower, hence inactive. As reported by [30], low ion activity makes the soil ion conductivity flow less and eventually decreases the EC of the soil. The soil texture could also be a reason for the low EC. The soil textural types were all sandy loam, dominated by sand. Sandy soil cannot hold moisture very well due to its low surface contact degree.

TABLE 1: Selected physicochemical properties of the soils.

Sample	pH (H ₂ O)	pH (KCl)	ΔpH	EC (mS/cm)	%OC	% OM	%N	C/N	Na ⁺ (cmolc/kg)	K ⁺ (cmolc/kg)	Ca ²⁺ (cmolc/kg)
MWC	5.0	4.0	-1.0	0.03	2.99	5.16	0.141	21	0.52	0.73	4.4
MWV	4.7	3.8	-0.2	0.02	3.55	6.12	0.167	22	0.71	1.96	4.08
MEC	5.1	4.1	-1.0	0.02	4.03	6.96	0.183	22	0.52	0.51	4.88
MEV	5.0	4.1	-0.9	0.01	4.17	7.20	0.224	19	0.52	1.21	3.6

Sample	Mg ²⁺ (cmolc/kg)	SB (cmolc/kg)	CEC (cmolc/kg)	Avail. P (mg/kg)	EA (cmolc/kg)	% Sand	% Silt	% Clay	A-Fe (mg/g soil)	Free Fe (mg/g soil)	A-Al (mg/g soil)	Free Al (mg/g soil)
MWC	1.36	7.01	31.84	5.81	0.26	66.5	25.0	8.5	0.01	3.50	0.21	2.51
MWV	1.12	7.89	27.76	6.19	0.26	55.5	27.0	17.5	0.61	8.35	0.87	7.00
MEC	2.00	7.90	43.04	5.47	0.25	65.0	33.5	11.5	0.00	3.66	0.82	2.52
MEV	1.28	6.60	40.64	6.97	0.25	55.5	35.0	9.5	0.51	8.31	0.38	7.50

ΔpH = net charge (pH KCl-pH H₂O), EC = electrical conductivity, OC = organic carbon, OM = organic matter, N = total nitrogen, C/N = mineralization, MWC = Meupi West Cultivated, MWV = Meupi West Virgin, MEC = Meupi East Cultivated, MEV = Meupi East Virgin, SB = sum of bases, CEC = cation exchange capacity, Avail. P = available phosphorus, A-Fe = amorphous iron, and A-Al = amorphous aluminium.

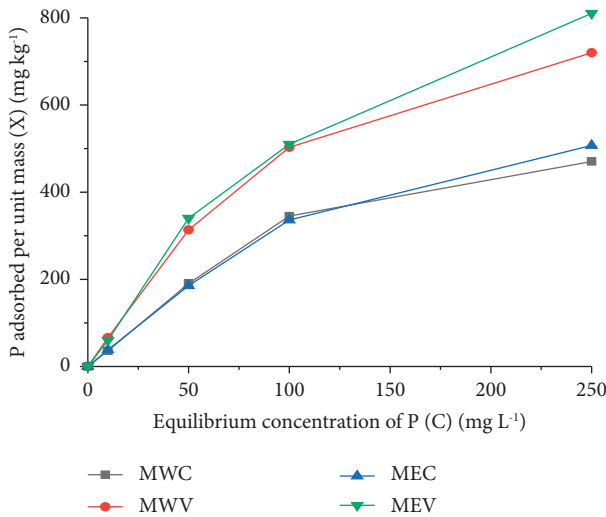


FIGURE 1: Phosphorus adsorbed as a function of the equilibrium concentration of the soil (24 hours equilibration at 25°C).

Soil organic matter levels in the soils were high as per the ratings established by [31]. MEV had the highest level of organic matter (7.20%), followed by MEC (6.98%), MWV (6.12%), and lastly MWC (5.12%). Total nitrogen content in all soils was low ($N < 1\%$) and ranged from 0.141 to 0.224%. C/N ratios were high (ranging from 19 to 22), indicating that the organic matter was poorly mineralized. Low soil N content and high C/N values could be attributed to immobilization and denitrification processes by soil bacteria.

Available phosphorus was low as per the ratings established by [26] and ranged from 5.47 mg/kg for MEC to 6.97 mg/kg for MEV. These low P concentrations may be associated with the acidic nature of the soil. At low pH values, Al, Fe, and Mn are highly soluble and will react with phosphate ions ($H_2PO_4^-$) to form hydroxyl phosphates, which are insoluble and unavailable for plants.

Exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) in all soil samples showed the following trend: $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. Quantitatively, the concentrations of these cations varied as follows: Ca^{2+} (between 3.6 and 4.88 cmolc/kg), Mg^{2+}

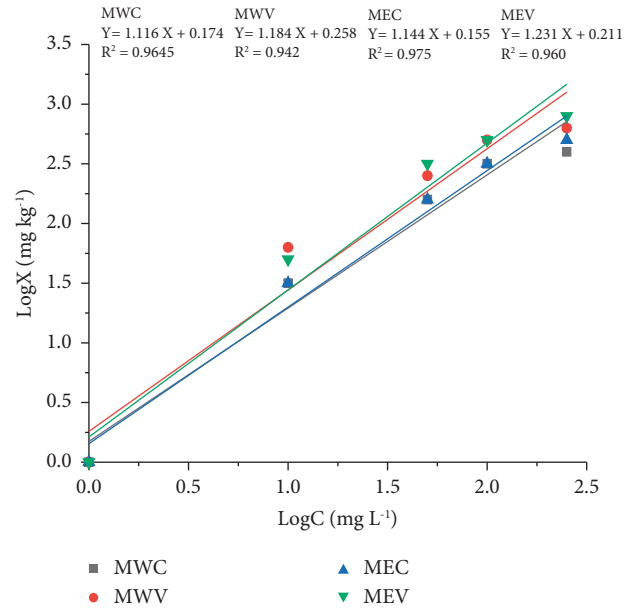


FIGURE 2: Linear Freundlich isotherm for the soil of Meupi (24 hours equilibration at 25°C).

(between 1.12 and 2.00 cmolc/kg), K^+ (between 0.51 and 1.96 cmolc/kg), and Na^+ (between 0.52 and 0.71 cmolc/kg). These concentrations were quite low (especially for K^+ , Na^+ , and Mg^{2+}) and varied from low to medium for Ca^{2+} based on the ratings established by [32]. These low concentrations may be due to the porous nature of the soils that are prone to base leaching. These low concentrations could also be explained by the prevalence of pH values of less than 5.5, where these cations are deficient.

Cation exchange capacity (CEC) ranged from 27.76 cmolc/kg for MWV to 43.04 cmolc/kg for MEC soils. The CECs of the soils were high as per the ratings established by [26]. These high CEC values indicate that the soil can retain and supply positively charged nutrient ions called cations. These include calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), ammonium (NH_4^+), and many of the

micronutrients [33]. Base saturation, which is the percentage of the soil CEC that is occupied by basic cations such as calcium, magnesium, potassium, and sodium at the current soil pH value, was less than 50% for all soils, showing that the soils studied are actually acidic in nature [14]. To increase the base saturation of these soils, lime is needed [32].

Particle size fraction indicated that the textural classes of the four soil samples were all sandy loam [34]. In all soil samples, the sand fraction was dominant followed by silt and lastly clay.

The concentrations of free and amorphous Al and Fe were low in most of the soils. Free and amorphous Al ranged from 2.51 to 7.50 mg/g soil and from 0.21 to 0.87 mg/g soil, respectively, while free and amorphous Fe ranged from 3.50 to 8.35 mg/g soil and from 0.00 to 0.61 mg/g soil, respectively. The concentrations of free Al and Fe were higher than those of amorphous Al and Fe. The virgin soils showed higher concentrations of free and amorphous Fe and Al than the cultivated soils. This was probably due to the use of nitrate and sulfate fertilizers on the cultivated soil. The nitrates and sulfates in these fertilizers react with Al^{3+} and Fe^{3+} , thereby reducing their availability in cultivated soils.

Results of P sorption studies revealed that the apparent equilibrium time for P adsorption in the soil was 24 hours. The behavior of P adsorbed as a function of the equilibrium concentration of P is presented in Figure 1.

Phosphorus adsorption was observed to be very high at the beginning, and this value increased with an increase in the concentration of added P. It was also observed that there were at least two adsorption phases for most of the soil samples. The first phase was rapid (adsorption of P), and the second phase was slow (converting P to a more firmly held form). This may correspond to the rapid adsorption phase and to the more firmly adsorbed phase. Each soil sample adsorbed P differently with maximum adsorption values of 470.5, 720.1, 507.4, and 810.3 mg kg^{-1} soil for MWC, MWV, MEC, and MEV soils, respectively. The virgin soil in each site had a higher capacity to adsorb P than the cultivated soils. This could be explained by the higher acidity (low pH) and higher contents of free and amorphous Fe and Al (Table 1) in the virgin soil compared to the cultivated soils, which enhance P adsorption.

The phosphorus adsorption maxima were determined by fitting the solution P concentrations and adsorbed P values into the isotherm equations. Figures 2–5 present the linearized plots for Freundlich, Langmuir, Temkin, and Van Huay adsorption isotherms, together with their coefficients of determination (R^2), for P sorption studies on the four soil samples, respectively.

The linear Freundlich adsorption isotherm that expresses the logarithm of P adsorbed as a function of the logarithm of P in the equilibrium solution is presented in Figure 2.

The goodness of fit of the model was ascertained by looking at the R^2 values (Table 2). Most of the plots gave a good fit for the Freundlich isotherm with coefficients of determination (R^2) > 0.90 for all four samples. Values of Freundlich adsorption binding energy (K_f) ranged from

1.492 mg kg^{-1} for MWC to 1.811 mg kg^{-1} for MWV. Binding energies obtained from the Freundlich isotherm equation showed that the virgin soils have a higher capacity to adsorb P than the cultivated soils. The exponential of the Freundlich adsorption energy ($1/n$) was greater than 0.5 for the analyzed soils and indicated that these soils had a high affinity for P.

The linear Langmuir adsorption isotherm that expresses the ratio of the equilibrium concentration of P adsorbed (X) as a function of the equilibrium concentration of P (C) is presented in Figure 3.

For the linear Langmuir isotherm, $R^2 < 0.9$ for all four soils analyzed and indicated nonapparent conformity of the P adsorbed data with the Langmuir model. Langmuir adsorption maximum (X_m) for the soil series revealed that the values of adsorption maximum from the Langmuir equation (714.28, 714.28, 666.66, and 1,073.40 mg kg^{-1} soil for MWC, MWV, MEC, and MEV, respectively) were higher than the actual values (470.5, 720.1, 507.4, and 810.3 mg kg^{-1} soil for MWC, MWV, MEC, and MEV, respectively). This shows that all adsorption sites were not occupied by the adsorbate. The Langmuir adsorption binding energy (K_L) was high for the virgin soil compared to the cultivated soils and this indicated that the soil had a high capacity to fix P.

Temkin linear adsorption isotherms that express P adsorbed as a function of the natural logarithm of equilibrium concentration are presented in Figure 4.

All plots did not give a good fit with the Temkin isotherm ($R^2 < 0.9$). The buffering capacity (b), in the Temkin equation, was high for all soils with values ranging from 87.146 mL g^{-1} for MWC to 143.920 mL g^{-1} for MEV. The P adsorbed by Temkin model (a) was high for most of the soils with the highest value obtained for MEV. The virgin soils had a higher buffering capacity than the cultivated soils. The higher the buffering capacity, the higher the sorption capacity of the soil.

Van Huay linear adsorption isotherms that express P adsorbed as a function of the square root of equilibrium concentration are presented in Figure 5.

All plots gave a good fit with the Van Huay isotherm ($R^2 > 0.9$). The sorption coefficient (n) ranged from 32.26 L kg^{-1} for MWC to 54.04 L kg^{-1} .

Results of phosphorus adsorption parameters are presented in Table 2.

Kinetics of P from the solution showed that the sorption of phosphate ions from the solution onto the soil was relatively rapid in the first 12 hours and progressively diminished towards the apparent equilibrium time (24 hours). Amongst the various kinetic models such as the pseudo-first-second-order kinetic model and intraparticle diffusion model, the pseudo-second-order kinetics (PSOK) was the best model that explained the sorption kinetics. The pseudo-second-order kinetics (PSOK) is given by

$$P_t = P_e - \left\{ \left(\frac{1}{K_f P_e^2} \right) \frac{P_t}{t} \right\}, \quad (10)$$

where P_t (mg kg^{-1}) is the amount of P adsorbed at time t (hours), P_e (mg kg^{-1}) is the amount of P adsorption at

TABLE 2: Values of Freundlich, Langmuir, Temkin, and Van Huay constants and multiple coefficients determination (R^2) of the soils.

Code	Freundlich		Langmuir			Temkin			Van Huay			
	1/n	K_F (mg kg ⁻¹)	R^2	K_L (L mg ⁻¹)	X_m (mg kg ⁻¹)	R^2	b (mL g ⁻¹)	a (mg kg ⁻¹)	R^2	n (L kg ⁻¹)	m (mg kg ⁻¹)	R^2
MWC	1.116	1.492	0.965*	0.0100	684.93	0.704	87.146	-70.42	0.826	32.26	-24.52	0.969*
MWV	1.184	1.811	0.942*	0.0140	892.86	0.831	131.670	-100.75	0.842	48.60	-30.27	0.981*
MEC	1.144	1.428	0.975*	0.0105	666.67	0.732	90.322	-75.59	0.800	34.15	-33.17	0.978*
MEV	1.231	1.625	0.960*	0.0104	1,075.27	0.724	143.920	-116.36	0.817	54.04	-46.00	0.985*

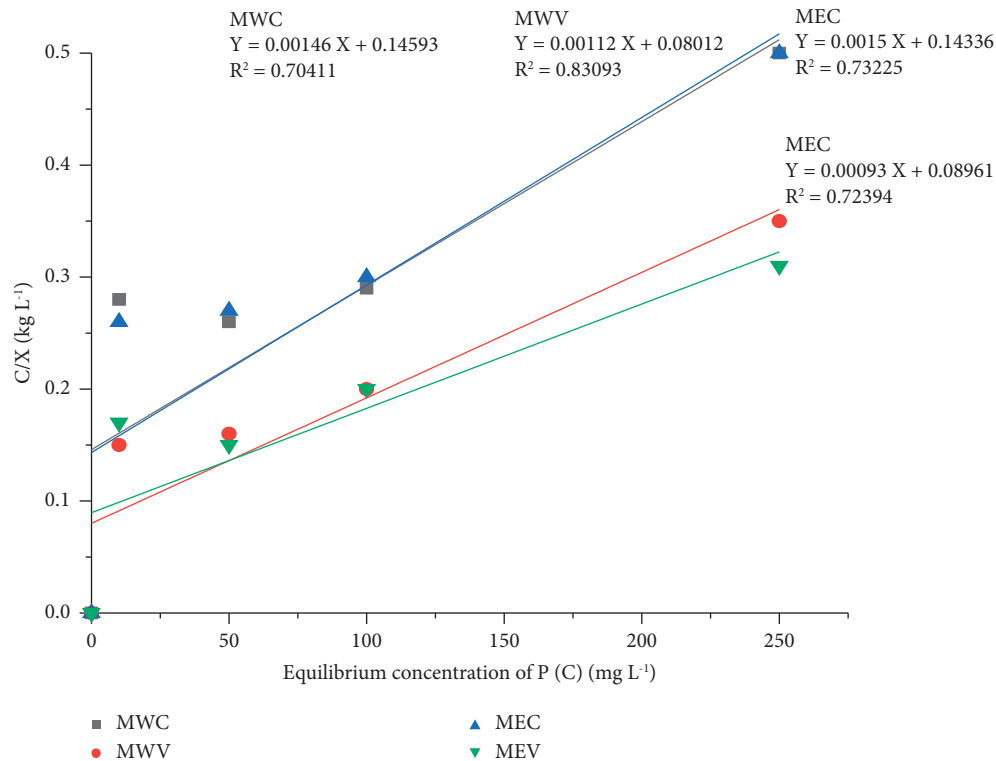


FIGURE 3: Linear Langmuir isotherm for the soils of Meupi (24 hours equilibration at 25°C).

equilibrium, and K' (kg mg⁻¹ h⁻¹) is the rate constant for the PSOK model.

Figure 6 represents the PSOK plot for soils from Meupi West Virgin.

The pseudo-second-order kinetics (PSOK) model gave a good fit to predict and describe P adsorption onto the selected soils with a coefficient of determination value (R^2) of 0.978. The pseudo-second-order kinetic constant, K' , was 0.049. The PSOK assumed that the phosphate sorption rate onto the soil depended on the number of available active sites, which is the driving force for phosphate sorption onto soil particle surfaces. Similar results were obtained by Chongqing et al. [35] while investigating Pb(II) sorption by biochar derived from *Cinnamomum camphora* and its improvement with ultrasound-assisted alkali activation.

The results of this study depicted that all four adsorption isotherm models could be used to describe and predict P fixation in the soils of Meupi. These soils have the capacity to fix P with the rate of P fixed increasing with added P. The adsorption isotherms showed different curves for each of the

soil samples. P fixation was site-specific, and the rates of P adsorbed on the soils were in the following order: MWC < MEC < MWV < MEV. The virgin soils showed higher levels of P fixation. After the P adsorbed data were inserted into the various adsorption models, it was observed that the models were able to describe the relationship between the capacity of the soil to fix P and P in the equilibrium soil solution. The accuracy of fitness (R^2) for the four models decreased in the following order: Freundlich isotherm > Van Huay isotherm > Temkin isotherm > Langmuir isotherm. Similar results have been reported elsewhere in Cameroon by [1,2,14].

Pearson correlation relationship (r) between soil physicochemical properties is presented in Table 3, while the Pearson correlation relationship between P adsorbed and some important soil physicochemical are presented in Table 4.

Correlation analysis between soil physicochemical properties (Table 3) revealed that significant negative correlations existed between exchangeable acidity and total

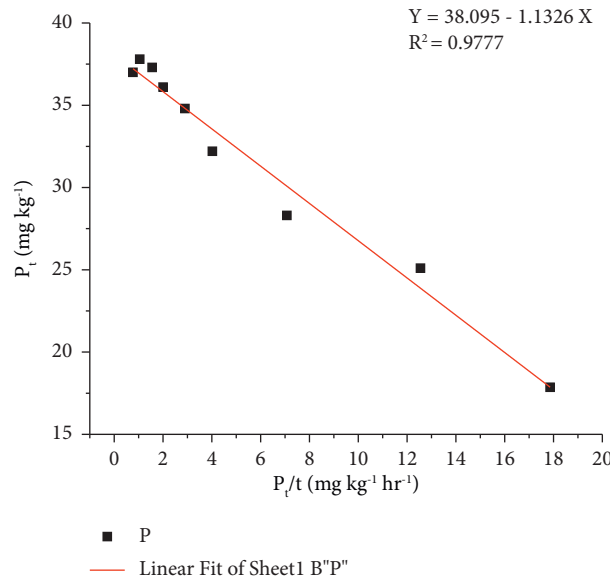


FIGURE 6: Experimental kinetic plot and fitting corresponding to the pseudo-second-order kinetic equation for the sorption of phosphate onto the soil chosen from Meupi West Virgin.

TABLE 3: Pearson product moment correlations between some important soil physicochemical properties.

	pH	EC	OM	N	SB	CEC	AP	EA	Silt	Clay	A-Fe	Free Fe	A-Al	Free Al
pH	1													
EC	0.001	1												
OM	0.275	-0.901	1											
N	0.219	-0.974*	0.920	1										
SB	-0.316	0.257	-0.012	-0.370	1									
CEC	0.838	-0.498	0.754	0.656	-0.188	1								
AP	-0.263	-0.735	0.380	0.693	-0.677	0.005	1							
EA	-0.667	0.707	-0.899	-0.822	0.177	-0.963*	-0.197	1						
Silt	0.504	-0.838	0.964*	0.915	-0.183	0.886	0.353	-0.978*	1					
Clay	-0.835	-0.101	0.043	-0.114	0.731	-0.528	-0.044	0.358	-0.223	1				
A-Fe	-0.754	-0.632	0.301	0.461	-0.090	-0.357	0.776	0.098	0.112	0.596	1			
Free Fe	-0.665	-0.716	0.391	0.564	-0.168	-0.248	0.834	-0.013	0.220	0.513	0.992**	1		
A-Al	-0.384	-0.213	0.388	0.074	0.887	-0.014	-0.304	-0.106	0.173	0.828	0.261	0.217	1	
Free Al	-0.612	-0.743	0.410	0.605	-0.245	-0.203	0.876	-0.054	0.258	0.440	0.980*	0.997**	0.150	1

*Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed).

TABLE 4: Pearson product moment correlations between some important soil physicochemical properties and phosphorus sorption parameters of the soils.

	pH	SB	AP	EA	Clay	Amorphous Fe	Free Fe	Amorphous Al	Free Al
$1/n$	-0.271	-0.349	0.894	-0.433	0.207	0.836	0.898	0.114	0.921
K_F	-0.941	0.113	0.553	0.426	0.758	0.932	0.879	0.329	0.844
K_L	-0.947	0.571	0.098	0.512	0.968*	0.697	0.608	0.661	0.541
X_m	0.110	-0.801	0.930	-0.476	-0.349	0.520	0.615	-0.434	0.678
b	-0.522	-0.299	0.905	-0.155	0.366	0.953*	0.984*	0.120	0.994**
a	0.402	0.361	-0.925	0.278	-0.267	-0.904	-0.951*	-0.079	-0.970*
n	-0.487	-0.309	0.909	-0.197	0.343	0.941	0.976*	0.118	0.988*
m	-0.198	0.465	-0.763	0.775	0.159	-0.492	-0.595	0.022	-0.642

*Correlation is significant at the 0.05 level (two-tailed). **Correlation is significant at the 0.01 level (two-tailed).

amorphous iron ($r=0.980, p<0.05$), and free aluminium and free iron ($r=0.997, p<0.01$).

Correlations between some important soil physicochemical properties and phosphorus sorption parameters of the soils (Table 4) showed that the capacity of the soil to adsorb phosphorus significantly correlated positively with amorphous Fe ($r=0.953$ and $p<0.05$), free Fe ($r=0.984, 0.976$ and $p<0.05$), free Al ($r=0.994$ and $p<0.01, r=0.988$ and $p<0.05$), and clay ($r=0.968$ and $p<0.05$). This shows that clay, free and amorphous iron, and aluminium are the main parameters considered predictors of phosphorus adsorption activity in the soils studied. These correlation results conform to those of Njoyim et al. [14] who studied the phosphorus adsorption isotherms in relation to soil characteristics of some selected volcanic-affected soils of Foumbot in the west region of Cameroon and Mbene et al. [1] who studied phosphorus fixation and its relationship with physicochemical properties of soils on the eastern flank of Mount Cameroon.

4. Conclusion

Results of soil physicochemical studies showed that the soils were strongly acidic (pH ranged from 4.7 to 5.1), with low available phosphorus (5.47 to 6.97 mg/kg). The apparent equilibrium time for phosphorus to be adsorbed in the analyzed soils was 24 hours. Phosphorus sorption studies revealed that the rate of phosphorus adsorption increased with an increase in the concentration of added phosphorus but decreased at a certain level at higher concentrations because the soil had no more capacity to adsorb phosphorus. The degree of fitness (R^2) of the phosphorus adsorption data for the different adsorption models was in the order Langmuir < Temkin < Van Huay < Freundlich. This suggested that the Freundlich isotherm model was the best fit to describe P sorption processes in soils. The pseudo-second-order kinetics (PSOK) model, which assumed that the rate of phosphorus sorption was dependent on the number of active sites, gave a good fit to predict and describe the kinetics of phosphorus sorption from the soil solution. The capacity of the soil to adsorb phosphorus significantly correlated positively with amorphous Fe ($r=0.953$ and $p<0.05$), free Fe ($r=0.984, 0.976$ and $p<0.05$), free Al ($r=0.994$ and $p<0.01, r=0.988$ and $p<0.05$), and clay ($r=0.968$ and $p<0.05$), which were the main parameters considered as predictors of phosphorus adsorption activities in the soils. The virgin soils (MWV and MEV) showed high P fixation and as such required more fertilization for optimum crop yields than the cultivated soils (MWC and MEC). Lime-induced immobilization of metals responsible for phosphorus sorption and mineralization of major nutrients will be useful to reduce soil acidity and unlock the phosphorus that is previously retained by the soil.

Data Availability

All relevant data have been included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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