Research Paper

Soil phosphorus adsorption characteristics and kinetics under different types of land use in Dire Inchine District, West Showa Zone, Oromia, Ethiopia

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Article Info	Abstract
	Soil phosphorus is an essential plant nutrient, and its insufficiency severely limits crop yields. However, its adsorption study plays a vital role in devising appropriate soil phosphorus, "P", management practices for its use proficiency. This study was initiated to evaluate phosphorous adsorption characteristics and kinetics of soil of three different land uses. A representative topsoil samples (0-20 cm) depth from the forest, grazing, and cultivated lands were collected and weighed 1g of composited soil samples were equilibrated in 20 ml of 0.01 M $CaCl_2$ solution containing KH_2PO_4 at rates of(0, 5, 25, 100, 150 and 250) mg P L^{-1} for assessment of Langmuir adsorption isotherm using batch type experiment. Then, the equilibration time was deduced from the kinetic experiment and fixed at 5 hours. The textural class of soils of forest land was clayey loam, whereas that of grazing and cultivated lands was clayey. Soil pH values under the three land uses were found to be strongly acidic. The experimental soils differed considerably in sorption characteristics under the three land uses. The highest mean value of the product of biding energy and sorption maximum (Kq_{max}) was recorded in the soil of cultivated land (1.08 Lmg^{-1}) followed by forest land soil (0.7313 Lmg^{-1}), while the lowest was recorded for the soil of grazing land (0.672 Lmg^{-1}), indicating considerable variation soil phosphorus adsorption characteristics under three land-uses. The value of the regression equation (R^2) indicated that higher values ($R^2 > 0.9864$) have better soil binding strength than the others. Thus, the good fitness of the model was ascertained by witnessing the R^2 values. The kinetic data showed that the values of concentration of soil "P" adsorbed (q_e) under the three land uses were closer and the R^2 values were comparably lower and almost analogous for the pseudo 1st order kinetic model than the pseudo 2nd order model. Soil "P" sorption kinetics was fast in the first 120 minutes and then showed no change with the increase of the contact time.

1. Introduction

Soil deprivation and acidification are mainly caused by unsustainable land use management practices. Appropriate land use management practices have significant influences on soil quality indicators, particularly at the surface horizon (Wakene and Heluf, 2003). A study by Achalu et al., (2012) observed that changes in land use, particularly the conversion of forest land to continuous cultivation land with low inputs and overall poor management practices, are the causes of the decline of soil nutrients and creation of the depletion of organic matter stock and intensification of soil acidity.

Phosphorus, "P", is one of the essential macronutrients that determine crop growth and productivity. However, its deficiency limits crop production in most agricultural areas of Ethiopian highlands (Bereket et al., 2018). Its deficiency is mainly due to the tight adsorption of "P" by Fe-, Al-

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oxides/hydroxides compounds in soil (Xavier et al., 2009; Jalali and Tabar, 2011; Asmare et al., 2015). As a result, soil "P" concentration and amount of plant available form of "P" in the soil are usually often inadequate to meet plant requirements (Bereket et al., 2018; Bati and Achalu, 2021). Moreover, soil solution "P" is usually quite low due to the complex interactions of phosphate with various soil components (Shen et al., 2011). This low "P" in soil solution becomes the major limitation on agricultural crop production and productivity (Achalu et al., 2013). It can also be attributed to its sorption with cations such as aluminum (Al) and iron (Fe) oxides in acid soils and precipitation reaction of "P" with calcium (Ca) in calcareous soils of arid and semi-arid regions (Zhang et al., 2005; Palomo et al., 2006; Kisinyo et al., 2014; Bati and Achalu, 2021). Soil "P" sorption is considered to be the most important process controlling "P" availability in soils. Phosphorus sorption is mainly studied by sorption isotherms which were historically initiated for evaluating its availability for crop uptake but have become popular for assessing the soil "P" mobility in the soil environmental system(Achalu et al., 2013). Sorption isotherm is a key in differentiating soils into their sorbing characteristics & practicing appropriate remedies based on the intensity of "P" sorption of a particular soil (Hargopal & Pritpal, 2011).

The intrinsic low soil "P" and its robust sorption properties turn large proportions of its concentration into unavailable forms aggravating the problem, and this becomes a severe challenge for consequential "P" uptake in acidic soil areas (Achalu et al., 2013; Achalu, 2014; Bereket et al., 2018). Many soil chemical processes are always in dynamics and their Kinetic chemical reactions are used to fully understand the vigorous interactions of plant nutrients with soils in a certain time scale (Scheidegger and Sparks, 1996; Pal, 2011; Mekdes et al., 2022). Knowledge of the kinetics of dynamic interactions of plant nutrients is important to determine how rapidly reactions reach equilibrium ((Liang et al., 2015). Even though soil "P" sorption capacity has been studied in some of the acidic soil areas, little attention has been given to studying soil P adsorption and the kinetics process. Therefore, to fill the gap, the present

study was initiated to characterize "P" sorption characteristics and its kinetics as affected by land use types and to provide an indication for effective management of soil "P" and valuable information regarding how "P" performs in soils and the forecasting of soil phosphate fertilization.

2. Materials and Methods

2.1. Site selection, soil sampling and preparation:

The potentiality of representativeness of land uses has been confirmed through reconnaissance surveys and before collecting targeted soil samples. Accordingly, three major representative land uses (forest, grazing and cultivated lands of upper, middle and lower slope positions of the study area) were identified (Figure 1). Replications of composited soil samples from 0-20 cm depth of each land use was collected, dried, sieved, prepared, labeled, and transported for laboratory analysis.

2.2. Soil Laboratory Analysis and Determination:

Composited soil sample of 0-20 cm depth from each land use was collected for the determination of targeted parameters of soil properties. Soil texture was measured by the Bouyoucos hydrometer method as described by Day (1965). Soil bulk density was determined from undisturbed soil samples collected using a core sampler. An average value of soil particle density of 2.65g cm-3 was considered for the calculation of total soil porosity. The total porosity was estimated from bulk and particle densities as described by Brady and Weil (2016) (Equation 1).

Total porosity (%) = (1- Db/Pd) x 100   (1)

where: Db = bulk density in (g.cm^{-3}) and Pd = particle density (g.cm^{-3})

Soil pH was measured using a digital pH meter as a suspension of a 1:2.5 soil-water ratio (Baruah and Barthakur, 1997). Soil organic carbon (OC) was determined by the oxidation method (Baruah and Barthakur, 1997). Soil Total N was determined using the micro-Kjeldahl digestion procedure as designated by (Bremner and Mulvaney, 1982). Soil available "P" was analyzed using the Bray II method (Bray and Kurtz, 1945) and the interpretation was computed by using a spectrophotometer at a wavelength of 880 nm.
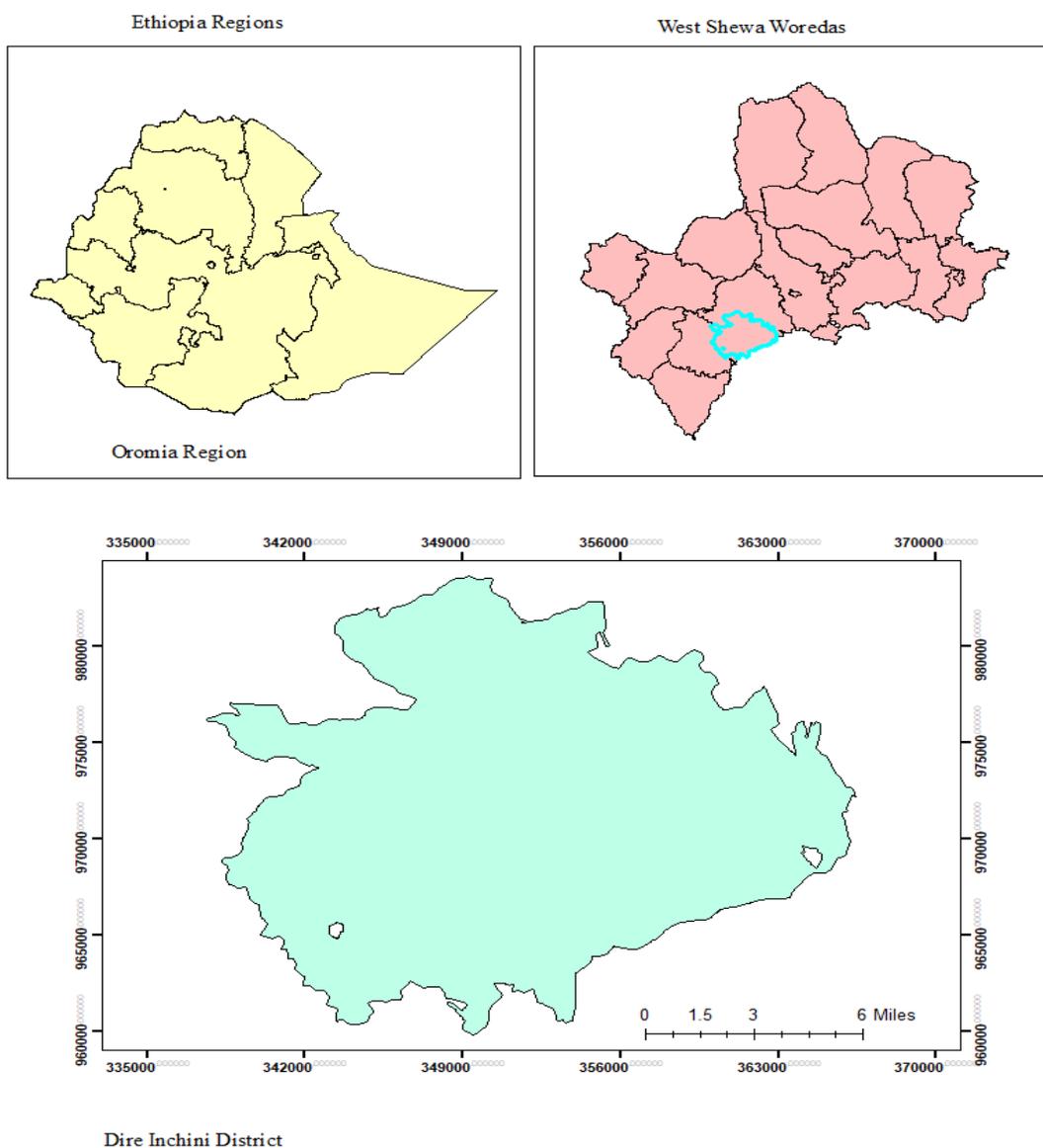
Ethiopia Regions

West Shewa Woredas

Oromia Region

Dire Inchini District

Figure 1: Location map of the study area

2.3. Langmuir phosphorus adsorption study of experimental soils

Soil "P" sorption study was determined by batch type experiment in which soil samples were agitated with "P" solutions of known concentrations (Graetz and Nair, 2008; Achalu, 2022). To measure the soil "P" sorption features, replicas of one gram of air-dried soil samples of the three land uses were equilibrated in 20 ml of 0.01 M $CaCl_2$ solution containing KH_2PO_4 at rates 0, 5, 25, 100, 150, and 250 mg P L^{-1} for 24 hours using mechanical shaker and batch type technique. From 2-3 drops of $CHCl_3$ were supplemented to abolish microbial growth (Self-

Davis et al., 2000). At end of the equilibration period, soil suspensions were centrifuged at 5000 rpm for 20 minutes, and then the adsorptive soil solution was separated from the adsorbent by centrifugation followed by filtration using a 0.45 μm membrane filter (Achalu, 2022). The filtered solution was then taken for measurement of the concentration of the initial available "P" sorbed using a spectrophotometer at a wavelength of 880 nm (John, 2009). Numerous models have been used to describe investigational data for sorption isotherms. Amongst these, the Langmuir isotherm model was used for this particular study. Attained sorption data were fitted to the Langmuir equation isotherm (Equation 2). The

quantity of added "P" sorbed by the soil (S`) was calculated from the difference between "Concentration in the equilibrium solution and the initial "P" added to the soil. To stabilize "P" sorption with pH, the experiment was conducted at the natural pH of the soils of each land use. Lastly, equilibrium data were examined and fitted with the Langmuir sorption isotherm equation (López-Luna et al., 2019).Statistical analysis

$$q_e = \frac{q_{\max}K_L C_e}{1 + K_L C_e} \qquad (2)$$

Where: q_e (mg/L) = concentration of soil "P" adsorbed on the unit mass of adsorbent, C_e (mgL^{-1}) = concentration of soil "P" at equilibrium, q_{max} (mg/L) = maximum adsorption capacity of the soil based on Langmuir equation, *and K* = Langmuir equilibrium adsorption constant (Lmg^{-1}).

2.4. Kinetics of soil chemical reactions under different land use types:

Many soil chemical processes are time-dependent (Scheidegger and Sparks, 1996). Such a study helps to fully understand, the dynamic nature and interactions of plant nutrients with soils and to predict their fate with time. Knowledge of the kinetics study is important to determine how rapidly reactions attain equilibrium and to infer evidence on reaction mechanisms. For the kinetic study of soils of different land uses, equilibration time was deduced from the kinetic trial and fixed at 5hrs. Soil chemical reactions occur over a wide time scale ranging from milliseconds for some sorption reactions to even years (Bereket et al., 2018; Bera et al., 2006; López-Luna et al., 2019). To study the adsorption mechanism, the kinetics of soil "P" soprion-adsorption was examined using pseudo1st order and pseudo 2nd order rate equations shown in equations (3) and (4) below.

$$q_t = q_e(1 - \exp^{(-k_1 t)}) \qquad (3)$$

$$q_t = \frac{(k_2 q_e^2 t)}{(1 + k_2 q_e t)} \qquad (4)$$

Where: q_t (mg/L) = amount of soil "P" adsorbed per unit mass of adsorbent at time t (hrs), q_e (mg/L) = amount of soil "P" adsorbed per unit mass of adsorbents at equilibrium, K_1(hr^{-1}) = pseudo-first-order rate constant, and K_2 (min^{-1}) = pseudo-second-order rate constant.

3. Results and Discussion

3.1. Status of selected soil properties under different land use types

The mean values of selected soil properties of the soils of the three land use types are indicated in Tables 1 and 2. The textural class of soils of forest land was clayey loam, whereas that of grazing and cultivated lands was clayey. The indication of clayey loam textural class in forest land is probably due to the presence of high organic matter in soil and the similarity of a textural class of clayey in grazing and cultivated lands may be due to similarity in the parent materials of the soils. Soil bulk density in the forest land was higher than the remaining land uses (Table 1). The lower & higher bulk density of soils in cultivated and forest lands may be accredited to the high SOM, porosity, and less soil disturbance in the forest land. Relatively, the total porosity was higher in forest land & lower in cultivated land. The fairly lower total porosity in soils of cultivated land when compared to natural forest & grazing land probably interrelated to high soil compaction & loss of SOM may be conveyed on the intensity of soil management practices thereby subsequent decrement of porosity than soils of forest & grazing lands.

Soil pH is a major soil parameter that regulates most of the biochemical reactions taking place in soils. It also indicates the degree of the availability of crop nutrients and lime requirement of soils. As per the rating by Jones (2003), soil pH values perceived in the three land uses were found to be strongly acidic soil. However, soil pH was relatively lower in cultivated land. Depletion of basic exchangeable cations in crop harvest leads to a release of H$^+$ ion to the soil solution and hence lowers the soil pH value in cultivated land than the remaining land uses.

Table 1. Mean values of selected physical properties of experimental soils

Land uses	Soil parameters						
	Sand (%)	Silt (%)	Clay (%)	Textural class	Bulk density (g/cm^3)	Total Porosity (%)	
Forest land	24.72	40.12	35.14	Clay loam	1.41	53.21	
Grazing land	19.35	35.15	45.15	Clayey	1.39	52.45	
Cultivated land	22.18	27.41	50.41	Clayey	1.38	52.07	

Table 2. Mean values of organic matter, total N, C: N ratio and available Phosphorus "P" content

Land uses	Soil parameters				
	pH(H$_2$O)	Organic Carbon (%)	Total Nitrogen (%)	C: N ratio	Available Phosphorus (mg kg-1)
Forest land	5.50	4.95	0.34	14.55	7.51
Grazing land	5.39	4.63	0.27	17.15	6.03
Cultivated land	5.27	4.21	0.22	19.14	5.67

The soils used for the present study recorded better percent soil organic carbon (OC) content for the forest land and lower in the cultivated land. The relatively better higher percent OC content in the forest land and lower percent OC in the cultivated land is attributed to plant litter fall which abundantly returns to the soil surface, thereby enhancing OC content in the forest land. The soil total N followed the same manner as that of the distribution of OC content. When an assessment is made among the land uses, the relatively lower organic OC and the total N in the cultivated and grazing lands could arise from the decline in OM inputs due to the removal of biomass during cultivation and grazing. Therefore, land use changes from forest land to grazing and then to cultivated land have caused deterioration of soil OC and total N content on the upper soil surface. The distribution of soil C: N ratio followed the same manner as that of soil OC and total N contents except for minor differences among the land uses. As per the rating of Cottenie (1980), the available "P" content of soils under the three land uses was succeeding for the medium range. The relatively lower available "P" content in grazing and cultivated lands may be due to the lower status of soil OC content.

3.2. Soil Phosphorus "P" sorption binding energy (K)

Soil "P" sorption bonding energy (K_L) values of the soil were highly affected by land-use types (Table 3).

The values ranged from 0.096 (Lmg^{-1}) to 0.167 (Lmg^{-1}) where the relative minimum and maximum value was recorded from the soil of grazing and cultivated lands, respectively. The values of K for all soils were greater than 0.096 (Lmg^{-1}), suggesting that there is no danger of loss of "P" into the subsoil and the river water (McDowell and Sharpley, 2001). However, soil "P" sorption binding energy relatively varied among the land use types of the present study (Figure 2.).

3.3. Soil Phosphorus sorption characteristics

The "P" sorption data of soils under different land uses were plotted according to Langmuir equations. The data showed a promising fitness with the Langmuir equation ($R^2 > 0.986$) for all land uses. The adjusted R^2 values ranged from 0.9864 to 0.9966 for the Langmuir, suggesting a good model fit. Phosphorus sorption indices and correlation of the indices with the constant K were presented in Table 3 and Figure 2.

Soil "P" sorption capacity and binding energy to hold "P" were calculated from soil "P" concentrations at equilibrium and rates of sorbed "P" on unit masses of soil colloidal suspensions. In all three land uses, equilibrium "P" solution and per unit "P" sorption by soil colloids increased with the increment of soil "P" concentration. Equilibrium soil "P" concentrations and "P" sorbed on soils of different land use varied from each other and at different levels of "P" solutions. As shown in Figure 3 initially, at low "P" concentration, the

relationship was linear and at high concentration, it deviated from linearity. The linearity between equilibrium "P" concentrations versus the rate of final "P" concentration "P" after equilibrium was due to the large intermolecular distance between soil "P" anions, resulting in negligible mutual repulsion, and deviation from linearity designated that the binding strength of soil to "P" decreased with increase in soil superficial saturation with "P" (Fernandes & Coutinho, 1994; Bera et al., 2006). The amounts of the final concentration of

"P" sorbed by the soils after equilibriums of the three land use increased with an increase in the level of additional "P" in the soil solution. Among the land uses, soils of cultivated land sorbed the highest amount of soil "P" after equilibrium at any level of added "P", followed by those of forest and grazing lands. Due to differences in the brutality of soil "P" sorption, the values of sorption maximum calculated from Langmuir isotherms also differ among land uses.

Table 3. Mean values of Langmuir sorption parameters and R^2 values of the regression analysis

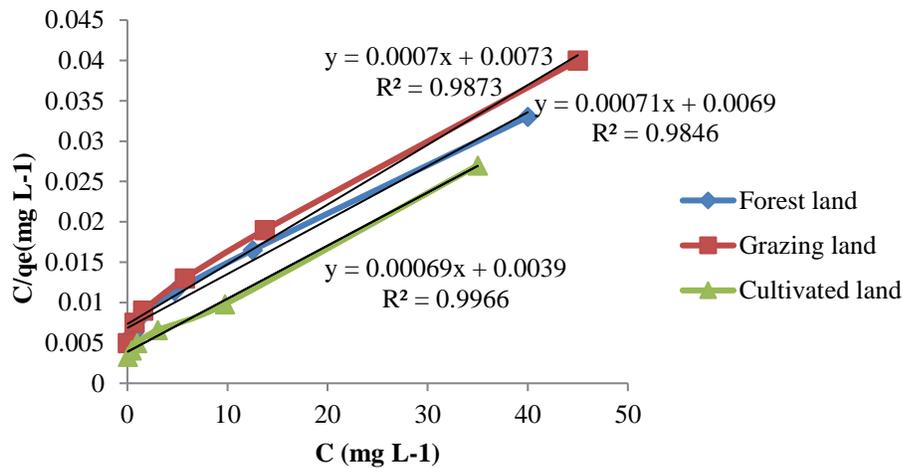| Land uses	q_e (mgL^{-1})	K_L(Lmg^{-1})	Regression equations	R^2	Kq_{max} (Lmg^{-1})	$1/q_{max}$
			Values of soil Phosphorus, "P", sorption characteristics and R^2 value			
Forest	9.72	0.103	Y=0.00071x+0.0069	0.9864	0.7313	7.10
Grazing	9.83	0.096	Y=0.0007x+0.0073	0.9873	0.672	7.00
Cultivated	19.05	0.167	Y=0.00069x+0.0039	0.9966	1.080	6.50

Figure 2: Fitness of the soil phosphorus "P" sorption isotherm to the Langmuir equation
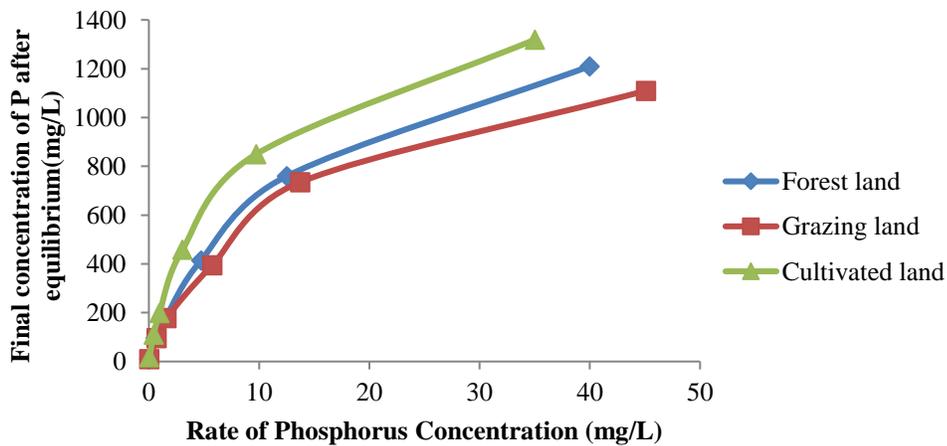

Figure 3: Langmuir "P" sorption isotherms of soils of different lands uses

3.4. Soil Phosphorus, "P", sorption indices, and orption maximum (Kq_{max}):

Regression coefficients (R^2) of Langmuir isotherm varied among the three land uses (Table 3) and ranged from 0.9864 to 0.9966 for the Langmuir isotherm. The soil "P" sorption behavior was described by the Langmuir sorption model with a regression coefficient ($R^2 > 0.9864$) observed for the soils of the three land uses (Table 3). However, when appraisals are made among land uses, soils differed noticeably in sorption characteristics under the three land uses. It is indicated that higher values ($R^2 > 0.9966$) have better strength than the lower values. Thus, the good fitness of the model was ascertained by witnessing the R^2 values. The highest mean value of the product of biding energy and sorption maximum (Kq_{max}) was recorded in the soil of cultivated land (1.08 Lmg^{-1}), followed by that of the forest land (0.7313 Lmg^{-1}), while the lowest was recorded for the soil of grazing land (0.672 Lmg^{-1}) (Table 3). The observed differences in the product of the binding energy and sorption maxima among the three land uses were most likely due to the differences in the amounts and nature of "Al" and "Fe" components present in the soils. In addition, the fairly higher product of biding energy and sorption maximum (Kq_{max}) in the cultivated lands could be partly due to the lack of residual effect of the application of external soil "P". This indicates that the studied soils might not be suitable for agricultural crop production. The relatively low production of the binding energy and sorption maxima in the grazing land could be due to better organic matter in the soils of this land than in the soils of cultivated land. Almost all the soils had sorption maxima ranging from (0.672 to 1.080 Lmg^{-1}), indicating that the soils have different sorption levels at different land uses.

3.5. Kinetics study of soil phosphorus adsorption

To examine the adsorption mechanism, the kinetics of soil "P" adsorption was analyzed using the pseudo1st order and pseudo2nd order rate equations described in equations (3) and (4) given above. The plot fit to the experimental data of soil "P" adsorption is given in Figure 5 and rate constants are summarized in Table 4.

The statistical criteria used for estimating the goodness-of-fit of the models to the experimental data were the coefficients of determination (R^2). The kinetic data show that $q_{e.exp}$ and $q_{e.cal}$ are closer, and the R^2 values are comparably lower and almost similar to the pseudo1st order kinetic model than the pseudo 2nd order model (Table 4). However, the R^2 values for the pseudo-second-order are high enough to fit the model. Moreover, the soils of the forest lands are very high enough to fit the model among the different land uses. The adsorption of soil "P" for this study is better described by pseudo 2nd order kinetics, the fairly higher ($R^2=0.9898$) value of the pseudo 2nd order kinetics recorded for the soil of the forest land, and the lower ($R^2=0.6999$) value was recorded in the grazing land.

3.6. Effect of contact time:

The effect of contact time between the originally sorbed and after equilibrium "P" of the soil of the forest, grazing, and cultivated lands is displayed in Figures 4 and 5. The adsorption at the beginning was fast at 1 hour under each land use type. After 180 minutes, there was no significant adsorption and it was almost static. Thus, 180 minutes of contact time is considered to be the equilibrium contact time for the batch study. At 320 minutes, which was the end of the adsorption, the experiment is not substantial to increase the time above 320 minutes. That is, there is no more soil "P" expected to be sorbed in the soils.

Table 4. Pseudo1st order and pseudo 2nd order kinetic model of soil phosphorus adsorption

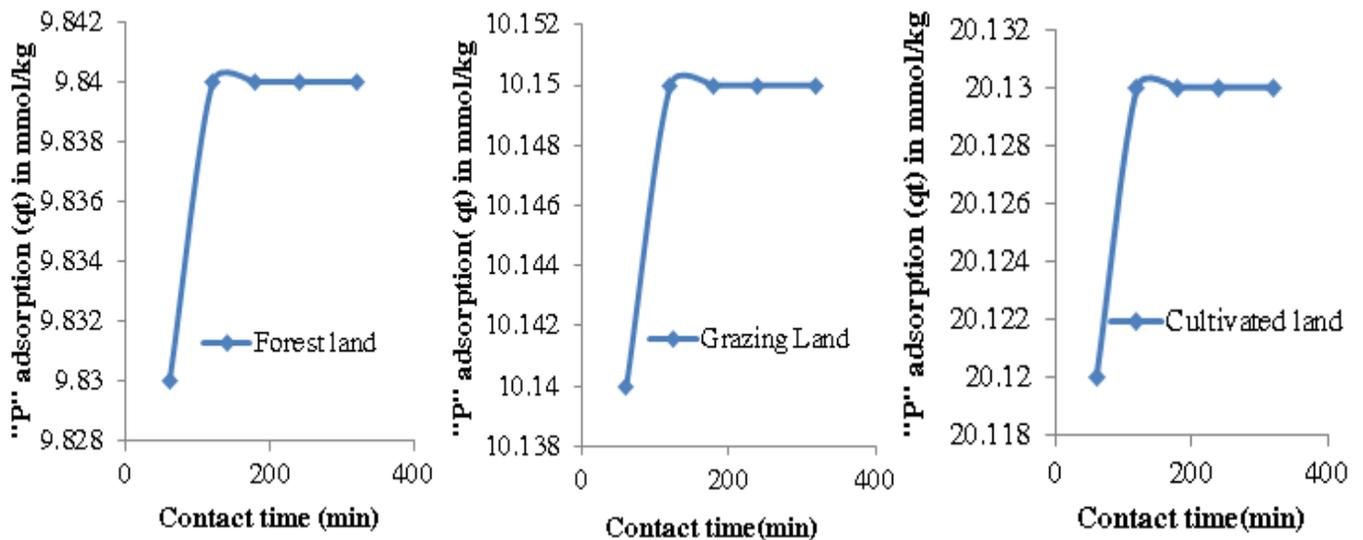| Land uses	q_e *exp.*(mmol/kg)	K_1, K_2 *(min^{-1})*	q_e (mmol/kg)	Pseudo-1st Order R^2	Pseudo-2nd Order R^2
Forest land	9.72	0.103	9.84	04674	0.9898
Grazing land	9.83	0.096	10.15	0.4674	0.6999
Cultivated land	19.05	0.167	20.13	0.4675	0.7911

Figure 4: Plot of Pseudo-1st order kinetic model of soil "P" adsorption under different land uses
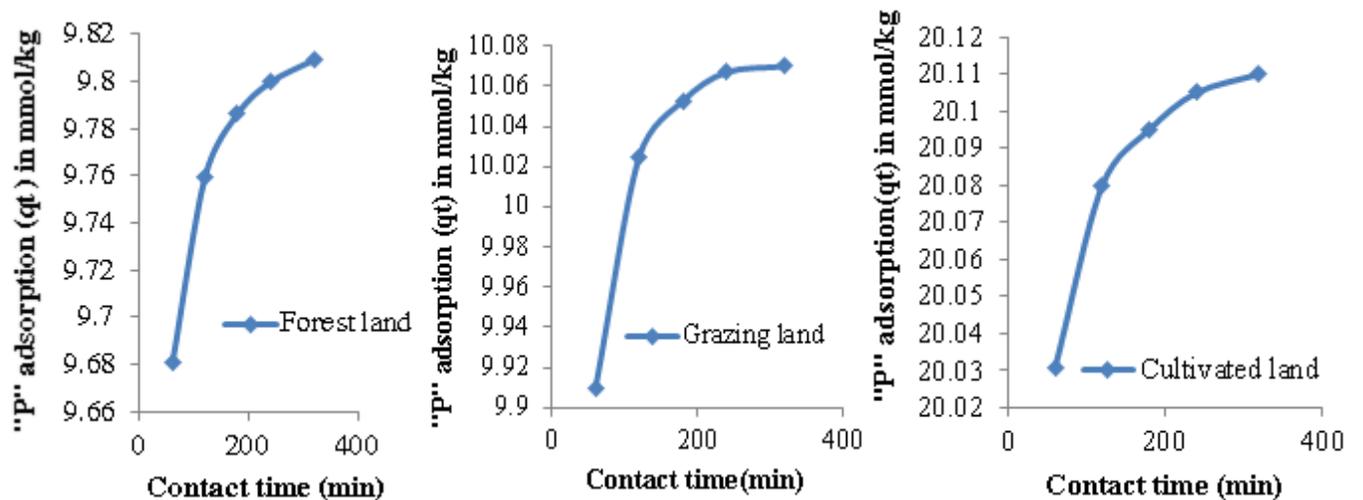

Figure 5: Plot of Pseudo 2nd order kinetic model of soil "P" adsorptions in different land uses

4. Conclusion

The results of the study revealed that soil pH under the three land uses fell under strongly acidic soil. However, significant differences in "P" sorption capacity and sorption characteristics were witnessed within land uses. The difference in soil "P" sorption characteristics under soils of different land uses brought variation in values of soil "P" binding strength, showing that higher values ($R^2 > 0.9864$) obligate better soil "P" binding strength. The highest mean value of the product of biding energy and sorption maximum (Kq_{max}) was recorded in the soil of cultivated land (1.08 Lmg^{-1}), followed by that of the forest land (0.7313 Lmg^{-1}), while the lowest was recorded in the soil of grazing land

(0.672 Lmg^{-1}). Thus, the good fitness of the model was ascertained by witnessing the relatively higher R^2 values. Langmuir model was found to be effective in describing the "P"-sorption patterns of soils of different land uses. The kinetic data indicated that the concentration of soil "P" adsorbed on the unit mass of adsorbent (q_e) of soil under different land uses are closer to each other, and the R^2 values are comparably lower and nearly referents for the pseudo1st order kinetic model than the pseudo 2nd order model. The "P" sorption kinetics in soils was fast in the first 120 minutes and then showed no variation with the increase of the contact time.

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