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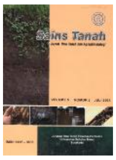

Determining the optimal application rate of chicken manure for agricultural land through Phosphorus sorption-desorption analyses in Andisols of Wonokitri, East Java, Indonesia

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ABSTRACT

Phosphorus (P) is a macro-essential element extensively used in agricultural production. Andisols, commonly found in Indonesia, serve as agricultural areas with high, excessive, and continuous organic matter input. However, the propensity of the soil for P leaching poses a potential risk of water pollution and eutrophication in the watershed area. This study aimed to evaluate the impact of the application rate of organic matter, specifically chicken manure, often employed in agricultural activities related to Andisols. The experiment involved observing P sorption, P desorption, P sorption kinetics, and P uptake by wheat (*Triticum aestivum*) in soil incubated with chicken manure added at various rates of 0, 10, 20, 30, and 40 t ha^{-1}. The incubation stages were conducted for 14 days at room temperature (27°C) and soil moisture was maintained within field capacity. The data collected were analyzed using Langmuir isotherm for P sorption and desorption, and first-order kinetics for P sorption kinetics. The results showed that the chicken manure addition at 10-40 t ha^{-1} significantly reduced P bonding energy in Andisols, but failed to decrease the sorption maxima value due to accumulated P from previous applications performed. The application of 20 t ha^{-1} (CM20) of chicken manure was found to be the optimal rate, displaying high P uptake and reduced bonding energy, while rates above 20 t ha^{-1} showed no significant difference in P uptake and bonding energy levels. Therefore, CM20 was recommended to increase P availability and prevent P movement into water bodies, promoting sustainable agricultural practices.

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1. INTRODUCTION

Andisols, occupying an area of 5.4 million hectares in Indonesia, are a soil type that plays a crucial role in food production, including potatoes and vegetables (Sukarman & Dariah, 2014). However, the main concern with Andisols is the limited availability of phosphorus (P). This deficiency is attributed to the transformation of available P to an unavailable form through P retention by minerals such as allophane, imogolite, and amorphous iron (Fe) and aluminum (Al) oxides (Anda & Dahlgren, 2020; Nash et al., 2014). Given their mineral-rich nature, Andisols possess high P sorption capacity, necessitating additional P for optimal plant productivity (Takamoto et al., 2021). P, being an essential element for living organisms, is extensively used in agriculture. The variable and uneven distribution of P in the soil can lead to its accumulation in unavailable forms for plants, posing a challenge to agricultural production, specifically in increasing and sustaining productivity (Velásquez et al., 2016).

Wonokitri, Pasuruan, situated near Bromo volcano in East Java, features Andisols, where farmers have attempted to improve P availability by applying P fertilizers along with chicken manure to the soil. The quantity of chicken manure applied varies among farmers, and this practice over the years has accompanied the escalating food demand. The continuous application of organic matter containing high P, such as chicken manure, may increase available P levels in the soil by reducing sorption site capacity (Pradhan et al., 2021). However, excessive application of chicken manure causes environmental adverse effects, particularly on water bodies. Considering that Andisols are generally situated in volcanic highlands with steep slopes, the potential environmental impact is amplified. Poore and Nemecek (2018) stated that 78% of eutrophication in water bodies emanated from food production practices, including fertilization. In steep areas, runoff processes significantly contribute to water pollution (Jwaideh et al., 2022). Previous studies showed significant effects of chicken manure application on plant growth (Dani et al., 2021; Pujiastuti et al., 2018; Thepsilvisut et al., 2022), while some suggested an increased tendency for environmental pollution (He et al., 2021; Yang et al., 2016). Studies investigating the impact of agricultural activities, such as manure application, on P status in tropical Andisols of Indonesia indicated a reduction in P retention and an increase in total P and P availability (Anda & Dahlgren, 2020; Anda et al., 2021). There is less exploration of the optimal limit of manure application rate in tropical Andisols.

Evaluating the P sorption and desorption characteristics of Andisols in Wonokitri is crucial to ensure adequate P availability and environmental sustainability. Therefore, this study aimed to determine the optimal rate of chicken manure application on Andisols of Wonokitri through P sorption-desorption, P sorption kinetics, and P plant uptake analyses. The results can serve as practical and environmental guidelines for agricultural activities in the region.

2. MATERIAL AND METHODS

The soil samples were collected from Wonokitri Village, Tosari District, Pasuruan Regency, East Java, Indonesia, where Andisols were predominantly found. Furthermore, they were classified in the subgroup of soil known as Typic Hapludand (Soil Survey Staff, 2014). The sampling area served as an intensive agricultural region, with potatoes as the primary commodity. Before the incubation experiment, samples collected from the topsoil at a depth of 0-30 cm were subjected to initial physicochemical properties analysis. The soil nutrient status was assessed based on (Nyi et al., 2017). The bulk density (BD) was determined using the core method, while the texture was evaluated through the pipette method. Additionally, field capacity was determined by following the Alhricks method. The pH was measured with a 1:5 (w/v) H_2O and KCl solution using a pH meter (WTW inoLab pH 7110). The organic carbon (C) content was estimated with Walkley and Black method. Cation Exchange Capacity (CEC), exchangeable Calcium (Ca) and Magnesium (Mg), as well as Potassium (K) and Sodium (Na), were determined by extracting the soil with 1 mol L^{-1} of NH_4OAc at pH 7. These parameters were measured using the titration method, an Atomic Absorption Spectrophotometer (AAS) (AA-6300, Shimadzu Corporation), and a Flamephotometer (PFP7, Jenway), respectively. Available P was evaluated with the Bray 1 method, and total P was determined through a digestion method using concentrated HNO_3 and $HClO_4$. Exchangeable Al extracted from the soil with 1 M KCl was measured through the titration method. To identify the presence of amorphous Al and Fe, the soil was extracted with 0.2 M ammonium oxalic acid at pH 3 and evaluated using AAS. Moreover, the chemical properties of chicken manure were analyzed and organic C was calculated gravimetrically by employing the loss of ignition method. The total P content was extracted using the HNO_3 and $HClO_4$ digestion method, and pH was determined through H_2O extraction. The level of P in the manure was estimated using a UV-VIS Spectrophotometer (UV-1280, Shimadzu Corporation).

2.1. Incubation Experiment

The incubation experiment was conducted to evaluate the impact of different chicken manure application rates on P sorption-desorption in Andisols. A completely randomized design was employed with three replications for each treatment. The treatments included five different rates of chicken manure, namely CM0 (control/without chicken manure), CM10 (10 t ha^{-1}), CM20 (20 t ha^{-1}), CM30 (30 t ha^{-1}), and CM40 (40 t ha^{-1}). These rates were based on the typical application rate of chicken manure by local farmers, ranging from 20-30 t ha^{-1}.

Each incubation unit contained 200 g of soil mixed with the specified amount of chicken manure and placed in a 500 mL plastic jar. The respective manure amounts added to the 200 g soil were 0 g for CM 0, 1.37 g for CM10, 2.74 g for CM20, 4.11 g for CM30, and 5.4 g for CM40. There were three replicates for each treatment, leading to a total of 15 experimental units.

The plastic jars containing the soil-chicken manure mixtures were incubated for 2 weeks at room temperature (27**°C**). During the experiment, the soil moisture was maintained within field capacity by watering the jars every 2 days using gravimetric methods. In the course of incubation, the jars were covered to minimize evaporation. After the 2-week incubation period, the samples were collected, air-dried, and separated with a 2-mm sieve. The treated soil was employed for P sorption-desorption, P sorption kinetics, and P uptake.

2.2. Phosphorus Sorption and Desorption Experiment

A total of 3 g of the air-dried treated soil samples were saturated with 30 mL of 0.01 mol L^{-1} $CaCl_2$ containing P in the form of KH_2PO_4 at concentrations ranging from 0 to 300 mg kg^{-1}. The soil was incubated for 6 days at 27**°C** with regular shaking every morning and evening for 30 minutes, followed by centrifugation and filtration. P desorption was observed by shaking the soil with 28 mL of 0.01 mol L^{-1} $CaCl_2$, using the same centrifuge tube and incubation period previously employed for sorption observation. The concentration of P in the solution was measured using the molybdenum blue colorimetric method with a UV-VIS Spectrophotometer (UV-1280, Shimadzu Corporation, Japan) at 660 nm. Subsequently, the data were simulated using the following two-site Langmuir isotherm equation (Eq. 1).

$$x/m = \frac{k_1 b_1 C}{1+k_1 C} + \frac{k_2 b_2 C}{1+k_2 C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [1]$$

Notes: C represents the concentration of adsorbate in the solution at equilibrium (mg L^{-1}), x/m is the adsorbate absorbed per soil weight (mg kg^{-1}), k is a constant of bonding energy (mg L^{-1}), and b is the maximum P sorbed (mg kg^{-1}). The subscripts 1 and 2 refer to the first sorption site (part 1 with a lower C value) and the second sorption site (part 2 with a higher C value), respectively.

2.3. Phosphorus Sorption Kinetics

A total of 3 g treated soil samples were mixed with 30 mL of 0.01 M $CaCl_2$ containing 300 mg kg^{-1} P in a centrifuge tube. The mixture was shaken at 170 rpm for various periods (5, 20, 30 minutes, and 1, 3, 6, 12, and 60 hours) at 27**°C** to determine the kinetics of P sorption. The solution was filtered to estimate P content using the molybdenum blue colorimetric method. The data were simulated using the first-order kinetic equation (Eq. 2):

$$\text{P sorbed} = a(1 - e^{-Kt}) \quad [2]$$

Notes: a is the maximum P sorbed (mg kg^{-1}), K is the sorption rate constant (h^{-1}), and t is the shaking period.

2.4. Phosphorus Uptake by Plants

P uptake by plants was evaluated using wheat (*Triticum aestivum*) as an indicator. A total of 30 wheat seeds were grown in a cardboard bowl with a hole at the base and filled with 450 g sand, then stacked in a second one without holes. A nutrient solution containing 15 mg of Nitrogen (N) and 15 mg K was added to the sand media, followed by 40 mL of distilled water per cardboard bowl. On the 11th day of planting, the cardboard bowl with the growing plants was placed on top of another one containing 200 g of soil treated with chicken manure and incubated for 2 weeks. After being kept in the bowls for 3 more days, the plants and their roots in the sand media were harvested and rinsed with distilled water on the 3rd day. P in plant tissues was extracted using the digestion method with HNO_3 and $HClO_4$.

2.5. Statistical Analyses

The data obtained were processed with Microsoft Excel 2013 and Sigmaplot 14.0, and subjected to analysis of variance (ANOVA), followed by the Tukey Test at a 5% significance level using IBM SPSS software. Additionally, the Pearson correlation test was employed to determine the relationship between variables.

2.6. Criteria for Selecting the Optimum Application Rate of Chicken Manure

The criteria for selecting the optimum application rate of chicken manure included low P bonding energy in P sorption-desorption, a high percentage of P released in desorption analysis, a low constant rate of P sorption kinetics, and optimum P plant uptake.

3. RESULTS

3.1. Soil Physicochemical Characteristics

Table 1 shows physicochemical characteristics, indicating the presence of andic properties in the soil, consistent with the requirements of Andisols. The soil bulk density (BD) reached 0.73 g cm^{-3} and its estimated oxalate-extractable Al (Al-o) + ½ oxalate-extractable Fe (Fe-o) value was 3.92%, confirming the andic properties. The texture was identified as silty loam, comprising 21.0% clay, 66.0% silt, and 13.0% sand. The initial soil pH values in H_2O and KCl were highly acidic at a range of 4.31 and 3.82, respectively. The organic C content was 2.49%, showing a medium status based on the provided criteria. The CEC value was moderate at 24.3 cmol$_c$ kg^{-1}, while the soil base saturation was very low, measuring 19.3%. The soil samples exhibited low concentrations of basic cations, with exchangeable Ca at 2.84 cmol$_c$ kg^{-1} and Mg at 0.78 cmol$_c$ kg^{-1}. The concentrations of K and Na were classified as moderate, with values of 0.47 cmol$_c$ kg^{-1} and 0.61 cmol$_c$ kg^{-1}, respectively. The total P content was high, namely 2067 mg kg^{-1}, and the available P (P-Bray) content was very high, reaching 54.9 mg kg^{-1}.

3.2. Phosphorus Sorption

The results in Table 3 suggested the presence of two sorption sites with different affinities for P in Andisols. With the addition of chicken manure at rates of CM10, CM20, CM30, and CM40, the bonding energy values in the first sorption site consistently decreased by 50.7%, 80.3%, 83.3%, and 89.2%, respectively. The second site exhibited bonding energy reductions of 31.4%, 51.4%, 54.3%, and 63.9%, respectively, compared to the control (CM0). Among the treatments, CM20 was found to be the most optimum, as the differences in bonding energy values were not significant between CM40 and CM30. However, the addition of CM10-CM40 of chicken manure did not change the sorption maxima at all sorption sites.

Table 1. Soil physicochemical properties

Parameters	Value	Status
Bulk density (g cm^{-3})	0.73	-
Clay (%)	21.0	-
Silt (%)	66.0	-
Sand (%)	13.0	-
pH (H_2O)	4.31	VA
pH (KCl)	3.82	-
Organic C (%)	2.56	M
CEC (cmol$_c$ kg^{-1})	24.3	M
Base saturation (%)	19.3	VL
Exchangeable Ca (cmol$_c$ kg^{-1})	2.84	L
Exchangeable Mg (cmol$_c$ kg^{-1})	0.78	L
Exchangeable K (cmol$_c$ kg^{-1})	0.47	M
Exchangeable Na (cmol$_c$ kg^{-1})	0.61	M
Exchangeable Al (cmol$_c$ kg^{-1})	1.38	L
P-Bray (mg kg^{-1})	54.9	VH
Total P (mg kg^{-1})	2067	-
Al-o (%)	2.38	-
Fe-o (%)	3.08	-
Al-o + ½ Fe-o (%)	3.92	-
Field capacity (%)	53.4	-

Notes: The soil properties were categorized based on Nyi et al. (2017); VL= Very Low; L=Low; M=Medium; H=High; VH=Very High; VA=Very Acid; A= Acid; SA= Slightly Acid; N=Neutral; SAL=Slightly Alkaline; AL=Alkaline

Table 2. Chicken manure characteristics

Parameters	Value
pH (H_2O)	7.36
Organic C	43.0%
Total P	1.15%

Table 3. The bonding energy of P sorption by the soil

Treatments	k_1 (L mg^{-1})	k_2 (L mg^{-1})	r^2_1	r^2_2
CM0	203a	0.35a	0.83	0.98
CM10	100b	0.24b	0.91	0.97
CM20	40.0c	0.17c	0.86	0.97
CM30	34.0c	0.16c	0.89	0.98
CM40	22.0d	0.13c	0.84	0.94

Remarks: *Means followed by different letters in a column are significantly different (Tukey's test, P<0.05).

3.3. Phosphorus Desorption

In contrast to P sorption analysis, P desorption simulation indicated the presence of only one sorption site. Table 4 shows the results of the P desorption analysis conducted using the conventional Langmuir isotherm with one sorption site. With the addition of chicken manure at rates of CM10-CM40, the bonding energy values were reduced compared to CM0. The differences among CM10, CM20, CM30, and CM40 were insignificant, although there was a noticeable decreasing pattern in the bonding energy. In terms of the percentage of desorbed P, CM20 exhibited a higher value than CM0 and CM10, reaching 11.3%, while CM30 and CM40 had relatively similar values compared to CM20.

3.4. Phosphorus Sorption Kinetics

Table 5 shows the results of the P sorption kinetics analysis. The addition of chicken manure at higher rates significantly affected the rate sorption constant of P in Andisols. Based on Figure 2, all treatments exhibited an initial rapid binding of P directly to the soil at the beginning of the experiment (5 minutes), followed by a gradual increase until reaching equilibrium at 12 hours. CM10 did not significantly differ from CM0, while the treatments with higher rates (CM20, CM30, and CM40) had significant differences compared to CM0. However, CM40 did not significantly differ from CM30 and CM0, leading to CM20 being identified as the optimum treatment for reducing the constant rate of P sorption.

3.5. Phosphorus Uptake by Plants

The analysis of P plant uptake, using wheat as an indicator to assess P availability in the soil, showed a significant effect of the addition. Based on Figure 3, compared to CM0, the rates of CM10-CM40 showed significantly higher P uptake results. CM20 displayed a particularly high increase in P uptake, reaching 425% compared to CM0. The highest rate, CM40, which caused only a marginal increase of 68 µg in P uptake, did not significantly differ from CM20 and CM30.

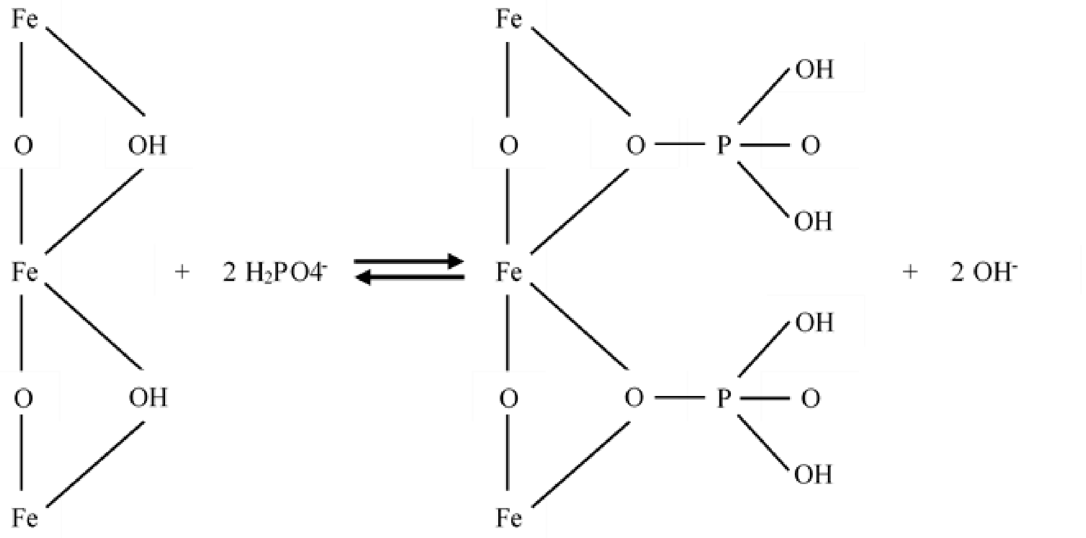

Figure 1. Ligand exchange mechanism in the soil due to the addition of $H_2PO_4^-$ (Hartono et al., 2018)

Table 4. Characteristics and percentage of P desorbed by the soil

Treatments	k (L mg^{-1})	r^2	P sorbed at 300 mg kg^{-1} P addition (mg P kg^{-1})	P desorbed at 300 mg kg^{-1} P addition (mg P kg^{-1})	% of P desorbed**
CM0	1.17a	0.99	3370a	216a	6.40
CM10	0.70b	0.99	3272b	225a	6.87
CM20	0.57b	0.99	3214c	362b	11.3
CM30	0.48b	0.99	3218c	409c	12.7
CM40	0.36b	0.99	3231bc	442c	13.7

Remarks: *Means followed by different letters in a column are significantly different (Tukey's test, P<0.05),
**Obtained by dividing desorbed P with P sorbed in an addition of 300 mg kg^{-1} P.

Table 5. The constant rate of P sorption simulated with first-order kinetics

Treatments	K (hour^{-1})	r^2
CM0	0.29a	0.87
CM10	0.29a	0.89
CM20	0.09b	0.81
CM30	0.14b	0.86
CM40	0.09b	0.83

Remarks: *Means followed by different letters in a column are significantly different (Tukey's test, P<0.05).

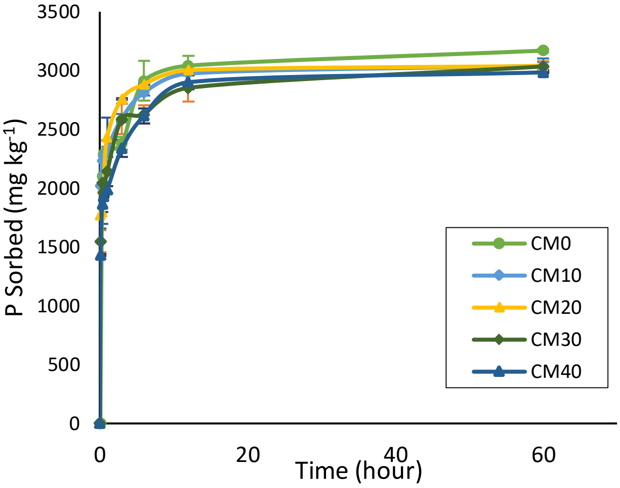

Figure 2. Phosphorus sorption kinetics by the soil samples

4. DISCUSSION

The sorption-desorption experiments showed that the addition of CM10-CM40 chicken manure in Andisols decreased the P bonding energy value, while the sorption maxima remained unchanged at both sorption sites once simulated with Langmuir isotherm. These results aligned with the previous report by Field et al. (1985) that chicken manure addition did not reduce the sorption maxima but caused a 33-41% decrease in the bonding energy. Many studies also stated that manure addition to the soil could reduce P sorption (Abdala et al., 2015; Nobile et al., 2020; Yang et al., 2019). The high P content in the applied chicken manure (Table 2) could decrease the soil bonding energy value by increasing its P saturation level. This potential was attributed to the very high available P levels in Andisols (Table 1) due to continuous and excessive fertilization with inorganic fertilizers or manure (Xu & Arai, 2022). In the sorption experiment, the highest treatment rate of CM40 showed similar results when compared to CM20, which was found to be sufficiently saturated with P

The high bonding energy value observed in the sorption-desorption experiment indicated a strong affinity of the soil for P. In the second site of this experiment, the bonding energy was lower than that of the first. This suggested that P bonding energy was not strong enough probably due to the accumulation of P in the soil from past fertilization and the current addition of chicken manure. Additionally, P desorption analysis showed only one sorption site when simulated with the Langmuir isotherm, meaning the desorption process mainly occurred at the second sorption site, which exhibited a lower bonding energy value.

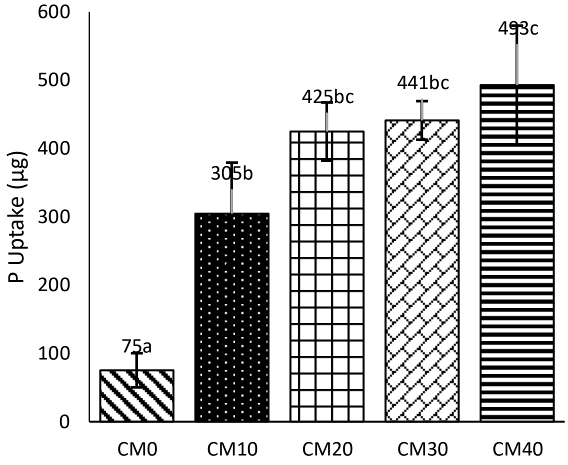

Figure 3. P Uptake by Wheat

In the second sorption site of the P sorption experiment (Table 3), there were no significant differences between CM40 and CM30 compared to CM20 in the bonding energy parameter. This observation suggested the P sorption site to have been saturated with the addition of CM20 chicken manure. P desorption experiments revealed that CM40 and CM30 increased the percentage of desorbed P by 1.00% and 2.40%, respectively. Meanwhile, CM20 caused a 4.43% increase compared to CM10, which was four times higher than the value observed from CM30 to CM40. A decrease in the percentage of desorbed P indicated P saturation in the soil, with the addition of higher rates of chicken manure being unable to elevate the percentage. Furthermore, rates exceeding CM20 in Andisols tended to cause pollution, as excessive manure application was included among the contributing factors to eutrophication through erosion and leaching (Jwaideh et al., 2022). Chen et al. (2022) showed that long-term application of high P rates at 395 kg P ha^{-1} yr^{-1} to the soil led to an unused amount of 338 kg P ha^{-1} yr^{-1}, boosting the potential for P loss and flow into water bodies.

The addition of organic matter, such as chicken manure with a high P content (P>0.3%), could influence complexation mechanisms and reduce the capacity of P sorption and retention (Yan et al., 2018); (Ghodszad et al., 2022). The $H_2PO_4^-$ in chicken manure might reduce the ability of the soil to absorb P through a ligand exchange, as shown in Figure 1. Additionally, its high organic C content (up to 43%) could decrease bonding energy through competition reactions among organic acids and P at soil sorption sites. The dissolution reactions and metal complexation reduced the absorption and retention ability, leading to increased available P (Urrutia et al., 2013). Dissolution reactions affect P availability by changing the structure of the adsorbent through the process of complexation and removal of Al and Fe. The addition of organic matter increased microbial activity in the soil, influencing P mineralization (Guppy et al., 2005; Tao et al., 2021). The moderate organic C content in the samples may be attributed to the stabilization of organic matter through the effects of allophane and Al and Fe oxides (Neculman et al., 2013). A drop in pH was observed to be initiated by the intensive management system and over-fertilization (Vašák et al., 2015).

Table 6. Correlation between variables

	K1 sorption	K2 sorption	K desorption	K sorption kinetics	P uptake
K1 sorption	1	0.980**	0.908**	0.815**	-0.953**
K2 sorption	0.980**	1	0.886**	0.804**	-0.935**
K desorption	0.908**	0.886**	1	0.709**	-0.877**
K sorption kinetics	0.815**	0.804**	0.709**	1	-0.787**
P uptake	-0.953**	-0.935**	-0.877**	-0.787**	1

Remarks: **Correlation is significant at the 0.01 level

Organic matter application was found to increase the pH, which was related to the P bonding energy value in acidic soil. The pH value affected the reaction of soil oxides, playing an important role in P sorption dynamics (Anda & Dahlgren, 2020). Andisols contained several minerals with a pH-dependent charge (Anda et al., 2021). Improvements in pH often contributed to increasing desorbed P and decreasing bonding energy (Nobile et al., 2020). Ghodszad et al. (2021) showed that the characteristics of P sorption and desorption depended on pH and organic C.

The addition of chicken manure to the soil influenced the constant rate of P sorption. P sorption kinetic analysis showed that the soil became saturated with P, thereby affecting the rate of P sorption, specifically at manure application rates above CM20. At higher treatments of CM20-CM40, the rate of P sorption decreased significantly, indicating that the sorption sites were saturated with P. According to Silva Rossi et al. (2016), the history of fertilization or P addition significantly affected the rate of P sorption through the binding mechanism of the soil sorption site. Consequently, the rate of P sorption influenced the optimal timing of fertilization (Guppy et al., 2005).

To validate the bonding energy values from the sorption-desorption experiment and the constant rate of P sorption, the actual uptake data by plants were needed. The addition of chicken manure led to increased P uptake by plants. Organic matter application could directly affect plant P uptake by increasing P availability and indirectly through improved soil structure, water-holding capacity, and root development (Guppy et al., 2005). The increased plant P uptake was attributed to rapid P mineralization in chicken manure (Islam et al., 2021). There was a negative correlation between P uptake and bonding energy as well as the rate of P sorption (Table 6). The result indicated that the addition of chicken manure decreased the P sorption rate constant and soil affinity for P.

The addition of chicken manure at high rates significantly reduced P bonding energy in Andisols, leading to increased P uptake by plants. However, the excessive application of chicken manure, specifically above CM20, could potentially cause environmental pollution through eutrophication. The optimal application rate of chicken manure in this experiment was found to be CM20, as it generated the optimal values for bonding energy, percentage of desorbed P, P sorption kinetics, and P uptake by plants.

5. CONCLUSION

In conclusion, CM20 was identified as the most optimal treatment in this study. This particular rate effectively reduced the soil bonding energy value and P sorption kinetics, while increasing the amount of desorbed P and P uptake by plants. However, the excessive application of chicken manure above CM20 should be avoided, as it could cause potential environmental pollution, specifically in water bodies.

Declaration of Competing Interest

The authors declare that no competing financial or personal interests that may appear and influence the work reported in this paper.

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