

# The Isothermal Phosphate Adsorption in a New Tidal Rice Field of Barito Kuala Regency South Kalimantan: A Study on Phosphorus Adsorption in Acid Sulfate Soils for Agricultural Improvement

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## ABSTRACT

High P adsorption reduces rice production, especially in newly reclaimed paddy fields. The research studied soil P adsorption using the adsorption isotherm equation and soil P solubility in a New Tidal Rice Field of Barito Kuala Regency. This incubation study used soil samples from Ray 7, Balandean Village, Alalak District, Barito Kuala Regency, South Kalimantan Province, from May to November 2022. The isothermal adsorption of P was measured in six soil samples with three replicates. P (0, 2, 5, 10, 15, 30, and 50 mg P kg<sup>-1</sup>) from KH<sub>2</sub>PO<sub>4</sub> were added in 1 g soil in 25 mL 0.01 M CaCl<sub>2</sub>. The suspensions were shaken at 25 °C for 17 hours, then centrifuged at 3000 rpm for five minutes, and the supernatant was filtered (Whatman 42) for P analysis. Three ordinary adsorption isotherm equations, Langmuir, Freundlich, and Brunauer-Emmett-Teller (BET), were used to fit the data. After adding 50 mg P kg<sup>-1</sup>, the average dissolved-P was 34.60 mg kg<sup>-1</sup> (69%), and adsorbed-P was 15.40 mg kg<sup>-1</sup> (31%). The BET equation was more suitable for describing P adsorption isotherm in this type of soil, which has the ability to adsorb one-third of any P addition.

**Keywords:** Acid sulfate soil, Al and Fe metals, Carbon, Isothermal phosphate adsorption, P solubility

## INTRODUCTION

Acid sulfate soils are found in tidal swamp land and are characterized by high soil acidity or low pH values. Soil acidity is one factor that makes acid sulfate soils infertile due to the low content of available nutrients and high levels of elements that are toxic to plants. Rice plants planted on them are often poisoned by Fe<sup>2+</sup>, organic acids, and H<sub>2</sub>S (Shamshuddin et al., 2013; Susilawati & Fahmi, 2013).

Acidic sulfate soil conditions (pH <3.5) make nutrients dissolve faster, and Fe concentration increases in rice field water (Shazana et al., 2014). Lime ameliorant application is an agronomic practice commonly used to reduce acidity and Al toxicity in acid soils. Amelioration with lime is an effective technology to improve 1) soil physical properties by increasing granulation to improve aeration, 2) soil chemical properties by reducing H, Fe, Al, and Mn

ions, and increasing the availability of Ca, Mg, and P), and 3) soil biological properties by increasing microbial activity (Ding et al., 2023; Koesrini et al., 2015). Liming has a beneficial effect on soil structure because it increases the stability of the soil structure (Quiroga et al., 2017).

Deficiency is one of the main factors inhibiting agricultural crop production (Kirkby & Johnston, 2008; Marschner, 2011). P deficiency is present worldwide and affects 42% of cultivated land (Liu et al., 1994). Fertilizer recommendations may result in the over-application of soil that would otherwise require less. P fertilizer is an expensive input, and the efficiency of its use by plants only ranges from 10-25% (Oliveira et al., 2018). Due to the high price of P fertilizer, it needs to be applied in the most efficient, effective, and economical way.

Making acid sulfate soils for rice fields is a wise choice because it can prevent the soil from oxidizing, which results in soil acidification (Bhakari et al., 2013; Noor, 2004). Sulfuric acid in soils, sediments, or substrates occurs naturally under waterlogged conditions (Michael, 2013; Wilson, 2005). If the

sulfide mineral as a sulfuric acid former has an enormous potential, it will have a terrible impact (Fitzpatrick et al., 2008; Michael, 2015). Acid sulfate soils develop due to the drainage of parent material rich in pyrite ( $\text{FeS}_2$ ) (Masulili, 2015; Mulyani & Sarwani, 2013), which can be improved by leaching to reduce the concentration of toxic compounds such as  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ , and soil acidity (Alwi et al., 2010; Ar-riza & Alwi, 2015).

Tidal swamp land has several limiting factors, such as acidity and soil toxicity due to high concentrations of Al and Fe, salinity, deficiency of nutrients such as P, and long-term high groundwater levels. The low availability of P nutrients is related to the low soil pH, which will increase the solubility of Al, Fe, and Mn ions that can absorb P by forming Al-P and Fe-P bonds (Kselik et al., 1992).

Many researchers have suggested using isothermal adsorption to determine the amount of P required to the optimum level for maximum crop yields (Fox & Kamprath, 1970; Holford, 1997). Several models have been developed (Kinniburgh, 1986; McGechan & Lewis, 2002) to quantitatively describe isothermal adsorption, the most popular of which are the Langmuir (Dossa et al., 2008; Essington, 2015; Pant & Reddy, 2001) and the Freundlich equation (Essington, 2015; Sparks, 2003).

The P uptake relationship is usually used to determine P needed by plants (EPR = External Phosphorus Requirement). EPR is the concentration of P in a solution that does not limit plant growth (Fox & Kamprath, 1970; Gichangi et al., 2008; Oyebanjo et al., 2022). For most plants, the amount of P in equilibrium with  $0.2 \text{ mg P L}^{-1}$  (EPR<sub>0.2</sub>) is a threshold at which no response to P is observed (Allen et al., 2001; Barrow & Debnath, 2014; Iyamuremye et al., 1996).

Considering the above facts, the main objectives of this study were (1) to provide insights into P adsorption from acid sulfate soils, (2) to identify the Al and Fe content associated with P adsorption in acid sulfate soils, and (3) to determine the adsorption process based on the common adsorption isotherm equations. These objectives were pursued to enhance the understanding of P adsorption in acid sulfate soils and to provide a basis for improving agricultural practices and environmental sustainability.

## MATERIALS AND METHODS

The research was a descriptive study of adsorption isotherms in the laboratory using soil samples from newly opened rice fields in Ray 7, Balandean Village, Alalak District, Barito Kuala

Regency, South Kalimantan Province. The research was conducted from May to November 2022. We used a standard incubation study method, adding varying amounts of P to soil samples and measuring the resulting P solubility and adsorption. This approach allowed us to determine the adsorption process and the most suitable isotherm equation for describing P adsorption in acid sulfate soils.

The soil samples were air-dried for two weeks, then crushed and sieved through a  $\text{Ø} 2 \text{ mm}$  sieve. A batch of 500 g of soil samples was prepared for isothermal adsorption analysis. Soil analysis was conducted at the Soil Chemistry Laboratory, Soil Department, Faculty of Agriculture, Lambung Mangkurat University, Banjarbaru.

The isothermal adsorption P was measured using this method (Erich et al., 2002; Morel et al., 1996; Yusran, 2005, 2010). Six soil samples with three replicates were added P (0, 2, 5, 10, 15, 30, and 50  $\text{mg P L}^{-1}$ ) in the form of  $\text{KH}_2\text{PO}_4$  into 1 g soil in 25 mL 0.01 M  $\text{CaCl}_2$ . Given the high P fixation capacity of acid sulfate soils, these concentrations were set in preliminary experiments to find a suitable concentration range. The suspension was shaken in a 50 mL centrifuge tube at 25 °C for 17 hours in a constant room. Tubes were centrifuged at 3000 rpm for five minutes, and the supernatant was filtered (Whatman #42) for P analysis. The P remaining in the solution after equilibration was measured using the Murphy and Riley Method (Asnandi et al., 2023; Rayment & Higginson, 1992; Yusran, 2005, 2010).

Three ordinary isothermal adsorption equations, Langmuir, Freundlich, and Brunauer-Emmett-Teller (BET), were used to fit the P adsorption data. The Langmuir equation, which is usually written as (Allen et al., 2001; Barrow & Debnath, 2014):

$$x = \frac{(K_L x_m c)}{(1 + K_L c)} \dots\dots\dots (1)$$

to become linear after rearrangement:

$$\frac{c}{x} = \frac{1}{K_L x_m} + \frac{1}{x_m} c \dots\dots\dots (2)$$

where  $c$  = P concentration in equilibrium solution ( $\mu\text{g P mL}^{-1}$ ),  $x$  = amount of P adsorbed ( $\mu\text{g P g}^{-1}$  soil),  $x_m$  = maximum adsorption ( $\text{ig P g}^{-1}$  soil), and  $K_L$  = related coefficient with bond energy. Therefore, the  $x/c$  versus  $c$  plot has a slope of  $1/x_m$  and an intercept of  $1/K_L x_m$ .

Freundlich's equation, which is usually written as:

$$x = K_F c^b \dots\dots\dots (3)$$

to become linear after log transformation:

$$\log X = \log K_f + b \log c \dots\dots\dots(4)$$

where *c* = concentration of P in the equilibrium solution (µg P mL<sup>-1</sup>), *x* = amount of adsorbed P (µg P g<sup>-1</sup> soil), *K<sub>f</sub>* and *b* = a constant where *K<sub>f</sub>* is a measure of the adsorption surface, and *b* relates to the adsorption energy (Allen et al., 2001). The log *x* versus log *c* plot has a slope *b* and a log *K<sub>f</sub>* intercept. Due to its simplicity, in which only two parameters can be adjusted, the Langmuir and Freundlich equations do not always match the experimental data obtained. The BET equation was applied to account for the plateaus, inflection points, and maxima observed in some of the data (Giles et al., 1974; Hinz, 2001). Unlike the Langmuir and Freundlich equations, classified as high-affinity adsorption equations, the BET equation is an adsorption equation that can explain the sigmoid isotherm, as observed for some of the data from this experiment.

The equation is usually written (Essington, 2015):

$$x = \frac{K_{BET} c x_m}{(c_s - c) \left( 1 + (K_{BET} - 1) \left( \frac{c}{c_s} \right) \right)} \dots\dots\dots(5)$$

As with the other two, this equation has a linear form after algebraic rearrangement:

$$\frac{c}{c_s - c} \cdot \frac{1}{x} = \frac{1}{K_{BET} x_m} + \left( \frac{K_{BET} - 1}{K_{BET} x_m} \right) \left( \frac{c}{c_s} \right) \dots\dots\dots(6)$$

where *c* = P concentration in the equilibrium solution (µg P mL<sup>-1</sup>), *c<sub>s</sub>* = solute concentration (i.e., soil), *x<sub>m</sub>* = maximum adsorption (µg P g<sup>-1</sup> soil), and *K<sub>BET</sub>* = interaction energy constant with soil particles. Therefore, the *c*/(*c<sub>s</sub>* - *c*) (1/*x*) versus *c*/(*c<sub>s</sub>* - *c*) plot has a slope (*K<sub>BET</sub>* - 1)/(*K<sub>BET</sub>* *x<sub>m</sub>*) and an intercept of 1/(*K<sub>BET</sub>* *x<sub>m</sub>*).

To determine the statistical significance of differences between equations, linear regression analysis with grouped data was performed on the data transformed to give a linear Langmuir, Freundlich, or BET relationship. This procedure allows for statistically significant values at the point of the isothermal adsorption.

### RESULTS AND DISCUSSION

Table 1 presents soil chemical properties from Ray 7 Balandean Village, Alalak District, Barito Kuala Regency.

The results showed that the adsorption isotherm of P was a quadratic model according to the law of diminishing return. By linearizing the Langmuir equation (2), a trendline graph of the relationship between *c*/*x* and *x* was obtained, as shown in Figure 1, with the equation *y* = 0.3178 + 0.0611*x* with *R*<sup>2</sup> = 0.926. The derivative of the above equation produced the parameters of the Langmuir equation, as presented in Table 2.

Table 1. Soil properties from Ray 7 Balandean Village, Alalak District, Barito Kuala Regency.

No	Properties	Value	Criteria*
Physic			
1	Sand %	18.97	
2	Silt %	44.32	Silty clay loam
3	Clay %	36.37	
Chemistry			
1	pH (H <sub>2</sub> O; 1:2,5)	3.58	Highly acid
2	CEC (cmol kg <sup>-1</sup> )	52.28	Very high
3	Organic-C (Walkley-Black, %)	4.47	High
4	P <sub>2</sub> O <sub>5</sub> (Bray, mg kg <sup>-1</sup> )	2.13	Very low
5	Total-N (Kjeldahl, %)	0.30	Adequate
6	Total-P (HCl 25%, mg 100 g <sup>-1</sup> )	34.96	Very high
7	Total-K (HCl 25%, mg 100 g <sup>-1</sup> )	22.16	Adequate
8	Soluble-Fe (ppm)	137.69	Very high
9	Exchangeable-Al (cmol kg <sup>-1</sup> )	5.81	Adequate

\* = Bogor Soil Research Center criteria (Balai Penelitian Tanah, 2005).

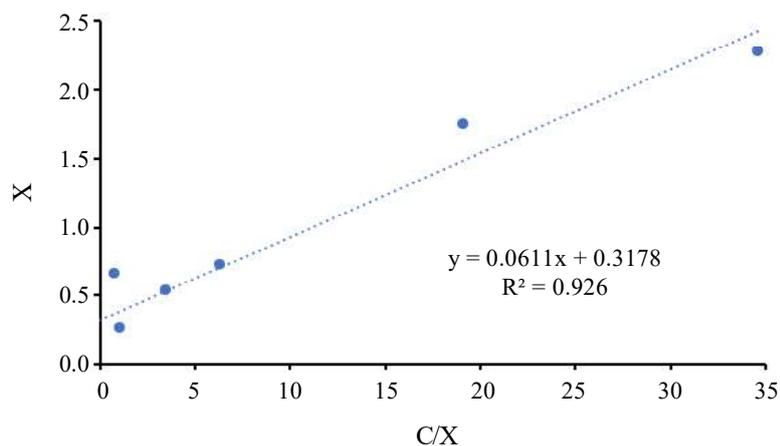


Figure 1. Linearized relationship between  $c/x$  and  $x$  in Langmuir equation.

Table 2. Langmuir parameters in soil samples from Balandean Village.

$x_m$ ( $\mu\text{g P g}^{-1}$ )	$K_L$	$R^2$
16.3666	0.1923	0.9260

Furthermore, calculations were performed using the Freundlich equation (4), which produced a graph of the linear relationship  $\log c$  with  $\log x$ , as shown in Figure 2. The trend line equation was  $y = 0.2955 + 0.6345x$  with  $R^2 = 0.8014$ . The derivative of the Freundlich equation produced the Freundlich parameters presented in Table 3.

Then, the curve fitting was continued using the BET equation (5), which produces a linear relationship between  $c/c_s$  and  $c/(c_s - c) \cdot i/x$ , as shown in Figure 3. The trend line equation was  $y = -0.0242 + 15.53x$  with  $R^2 = 0.975$ . The derivative of the BET equation is presented in Table 4.

P adsorption in soils with high Al and Fe content (Table 1) and acid sulfate soils highly depended on pH, organic matter content, and other elements such as Al and Fe. The essential nature of P adsorption can be used to estimate the management inputs if the soil's productivity is to be increased.

The high content of Al and Fe absorbs P nutrients. The high solubility of Al and Fe ions can fix P and cause poor plant growth (Dierolf et al., 2001). The P element in the soil is easily lost due to the leaching process, although some remains adsorbed on the surface of soil colloids. In most soils, maximum P availability is found in the pH range of 5.5-7.0. P

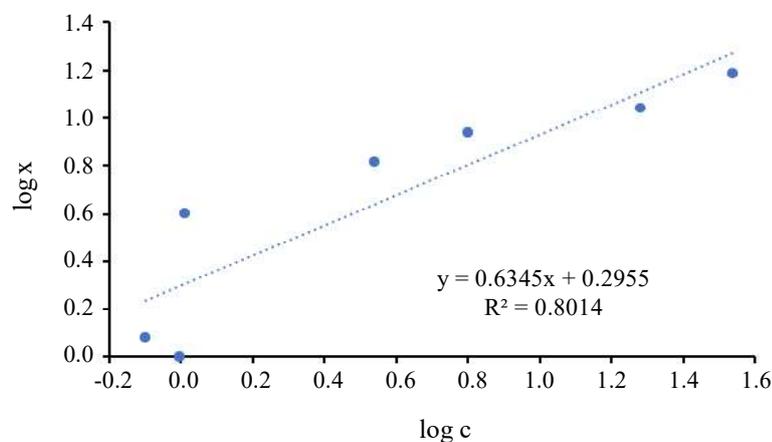


Figure 2. Linearized relationship between  $\log c$  and  $\log x$  in Freundlich equation.

Table 3. Freundlich parameters in soil samples from Balandean Village.

b	KF	R <sup>2</sup>
0.6345	1.9747	0.8014

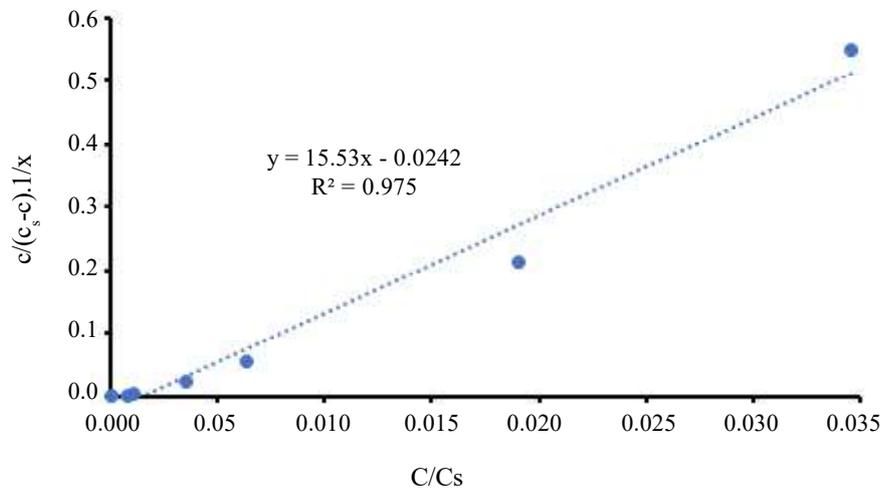


Figure 3. The linear relationship between  $c/c_s$  and  $c/(c_s - c) \cdot 1/x$  is in Brunauer-Emmett-Teller (BET) equation.

Table 4. Brunauer-Emmett-Teller (BET) parameters in soil samples from Balandean Village.

$X_m$ ( $\mu\text{g P g}^{-1}$ )	$K_{\text{BET}}$	R <sup>2</sup>
0.0645	-640.7000	0.9750

availability will decrease if soil pH is lower than 5.5 or higher than 7.0. The P uptake in the soil solution by Fe and Al-oxide can decrease if the pH increases. P is very susceptible to binding in both acidic and alkaline conditions. The longer P and soil contact, the more P is fixed. Over time, Fe will replace Al, so a form of Fe-P may be more difficult to dissolve than Al-P (Firmia, 2018).

The research results show that the amount of P absorbed by Al and Fe is predicted to increase with every increase in ppm P stock. However, the increase in P absorbed over time increases but is not significant. The amount of P absorbed increases, causing it and P to accumulate on the surface of Al-P and Fe-P, reaching equilibrium. High P uptake indicates low P availability. In other words, fixation activity in acidic mineral soil can result in less available P.

Analysis of P uptake and its relationship with isothermal adsorption in soil can be used in agriculture (Liu et al., 2019; Rahman et al., 2021). P uptake is useful for knowing the maximum P limit

available to the soil because of fixation by Al and Fe. Apart from that, the amount of P absorption can be used to determine the dose of lime and fertilizer so that it is not wasted. Isothermal adsorption is also helpful in treating Ultisol soil, which has an acid pH and Al and Fe content, which fixes P in the soil.

In this study, the average Dissolved-P after adding 50 mg P  $\text{kg}^{-1}$  was 34.60 mg  $\text{kg}^{-1}$  (69%), and Adsorbed-P was 15.40 mg  $\text{kg}^{-1}$  (31%). Meanwhile, the adsorption isotherm property of P was more accurately described by the BET equation compared to Langmuir and Freundlich. It resembled the linearization line of the equation and had the highest R<sup>2</sup> (0.9750, (Figure 3)). Seeing the adsorption that occurred, it can be said that the provision of P in the form of  $\text{KH}_2\text{PO}_4$  was absorbed by the sample soil around 30% (Figure 4). It could be affected by a higher content of soluble Fe in the soil as the affinity of Fe is thought to contribute to limiting available P in soils (Bai et al., 2021; Chacon et al., 2006; Lei et al., 2021). However, research by (Alia Farhana et al., 2017 Azman et al., 2014 and Sarwani et al., 2003)

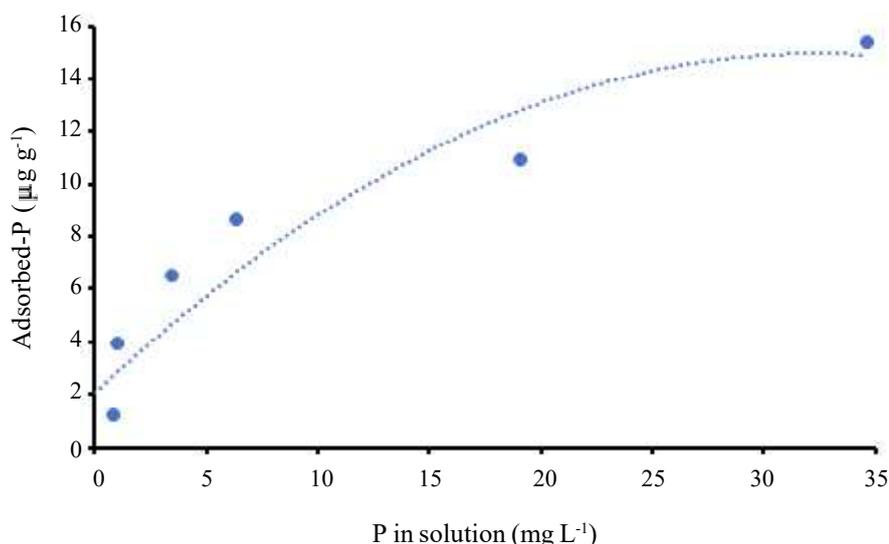


Figure 4. The relationship between P in solution and Adsorbed-P.

showed that the application of lime and organic matter reduced the solubility of Al and increased rice production in acid sulfate soils. It can be explained that ameliorants reduce the activity of Al and Fe (Sarwani et al., 2003) not to exceed the toxic threshold. Therefore, if the addition of P fertilizer is carried out, it must be accompanied by adding other ameliorants so that the concentration of P absorbed or fixed by the clay fraction can become available to plants (Koesrini et al., 2015).

## CONCLUSIONS

The modified method in measuring isothermal P adsorption in acid sulfate soil found that the maximum adsorption was about 31% from added P. The average Dissolved-P after adding 50 mg P kg<sup>-1</sup> was 34.60 mg kg<sup>-1</sup> (69%), and Adsorbed-P was 15.40 mg kg<sup>-1</sup> (31%) since the higher Soluble-Fe content in the soil. The BET equation was more suitable for describing the isothermal adsorption of P in this soil type than Langmuir's and Freundlich's. This soil needs amendment to overcome its high P adsorbing capacity before regular rice farming.

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