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The Influence of Fly Ash Application on the Sorption-Desorption of Phosphate on Raised-Bed Soil of Tidal Swamplands

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Abstract. The availability of phosphate (P) in soils generally is controlled by the sorption and desorption process of P ions by soil minerals. We examined the sorption and desorption of P on raised-bed soils of tidal swamplands applied with fly ash. Four different aged of raised-bed soils (3, 9, 16 and 27 years) was applied with 25 Mg ha⁻¹ fly ash, and incubated at the dark for 15 days, and a batch experiment was carried out following the completion of incubation for the measurement of sorption-desorption of P. Results of the study showed that P sorption to fly ash-added soils fitted very well to the Langmuir Equation ($R^2 = 0.91-0.98$), in which fly ash application increased the maximum capacity of soil for P sorption (Q_{max}). Increasing the value of Q_{max} might be attributed to the presence of aluminium and iron oxides containing in the fly ash increased the sites of fly ash-added soils for the P sorption. The amounts of phosphate released from fly ash-added soils ranged from 4.4% to 7.4% of sorbed P at the treatment of without fly ash addition. Fly ash addition to the soil significantly reduced the desorption of P. Results of this study imply the potential use of fly ash as waste material for improving P availability in the raised-bed soils of swamplands.

1. Introduction

Low level of phosphate availability for plants is generally main problem in agricultural cultivation in swamplands [1,2]. The low availability of P in swamplands is generally due to the low soil pH which causes increasing the solubility of Fe and Al, which may increase the fixation of phosphate [3,4]. Therefore, soil management is required to increase the availability of P for agricultural cultivation in swamplands.

The availability of phosphate in soils is controlled by the sorption and desorption process. The sorption of phosphate is a chemical process in soils in which orthophosphate ions react with absorbent materials in the soil so that they are absorbed in soil minerals and may reduce the leaching of orthophosphate ions [5,6]. Desorption of phosphate is the chemical process of orthophosphate release from sorption complex so that it could be absorbed by plants [7]. Thus, information on the sorption and desorption of phosphate in soils is substantially required for soil management to increase the efficiency of P fertilization.

Previous studies have shown that the application of ameliorant materials resulted in changes in the absorption and desorption of phosphate in soils [8,9]. Fly ash containing high amounts of Ca, Mg, Al, Fe, base metals and metal oxides [10,11] have been applied for soil pH improvement [12,13] and soil fertility preservation [14-16]. Fly ash is also used as an effective mineral sorbent for cleaning of petroleum spills [17,18]. The application of fly ash to soils might affect phosphorus sorption and desorption processes. Information about phosphorus sorption and desorption in soils is very important for improving the efficiency of phosphate fertilization in the raised-bed soils of tidal swamplands. Therefore, to obtain an understanding of the effect of fly ash application on the availability of P in the raised-bed soils, it is necessary to conduct research on the absorption and desorption of phosphate on the raised-bed soils applied with fly ash.

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2. Materials and Methods

2.1. Study site and soil sampling and characterization

Agricultural areas of tidal swamplands of the Desa Karang Indah, Sub-district of Mandastana, District of Bari² Kuala (3°09'56.6"-3° 10'41.0" S; 114°37'58.3"-114°39'51.4"E) have been chosen for this study. Soil samples were collected at the depth of 0-30 from four different ages of raised-soils: made in 2012 (3 years), 2006 (9 years), 1999 (16 years), and 1988 (27 years). The selection criteria for this study site are based on the consideration that all raised bed-soils used for this study originated from the same parent material, viz., sediment marine and are used for the same crop cultivation (rice in sunken-bed and fruit in raised-bed). After cleaning from the plant⁶ debris, soil samples were then air dried and stored until used for incubation experiments. Some of the soil samples were then air dried for determination of the physical and chemical properties of soil. The characteristics of soil used for this study are presented in Table 1.

2.2. Incubation and batch experiments

The application of fly ash to the raised-bed soils was done by adding fly ash equalled to the amount of 25 Mg ha⁻¹ to 100 grams of the raised-bed soil in a 200 mL experimental plastic pot. Soil and fly ash in the pot were mixed homogeneously, and water was added to obtain 60% water-filled pore space, and then incubated for 14 days. The plastic pot during the incubation period was covered with parafilm to avoid water loss through evaporation but still allows the exchange of oxygen in the plastic pots.

Batch experiment for phosphate sorption was carried out by reacting 0-175 mg P L⁻¹ phosphate solution with the raised-bed soils with and without the application of fly ash (Soil ratio: solution = 1:50) using a 50 mL centrifuge tube, then shaken in the dark for 12 hours. The suspension was centrifuged for 30 minutes at 2000 g and the supernatant was filtered through Whatman 42 filter paper. The phosphate concentration in the filtrate was then determined using the P-Bray I method [19]. The amount of phosphate absorbed is determined as the difference between the phosphate concentrations in the solution before and after equilibrium.

The amount of phosphate desorbed was measured using a phosphate-raised-bed soil association from the sorption experiment exposed using a phosphate-free solution having the same ionic composition and pH to the solution using in the phosphate sorption experiment. As much as 15 mL of desorption solution was added immediately to a phosphate-raised-bed soil association in a 50 mL centrifuge tube after the sorption experiment, centrifuged at 2000 g and decanted. The desorption solution was added to the soil in the same ratio as the sorption experiment, then shaken in the dark for 12 hours. The suspension was then centrifuged for 30 minutes at 2000 g and the supernatant was filtered through Whatman 42 filter paper. The phosphate concentration in the filtrate was determined using the P-Bray I method [19].

2.3. Statistical analysis

The phosphate sorption data is then fitted to the Langmuir⁸ equation using the least square curve fitting method in Microsoft Excel® [20]. Analysis of variance was carried out to determine the effect of coal ash application on sorption and desorption of phosphate onto different age of the raised-bed soils

using GenStat 12th Edition [21]. Least Significance Difference (LSD) Test was carried to differentiate the mean value of each treatment in the case result of variance analysis showed that the treatment had a significant effect.

3. Results and Discussion

3.1. Soil characteristics

Soils used for this study had a clay texture, with clay content varying from 65% to 70% (Table 1). High clay content in the raised-bed soils is predominantly caused by sludge lifted from the sunken beds and then deposited in the raised-bed which is carried out annually experiencing high clay contents. Thus, an accumulation of a layer of sludge containing clay occurs in raised bed soils.

Soil Characteristics	27 years	16 years	9 years	3 years
Soil texture (%)				
- Sand	1.05 ± 0.11 ¹⁾	0.85 ± 0.28	0.44 ± 0.08	0.47 ± 0.14
- Loam	33.32 ± 1.22	32.72 ± 1.26	32.92 ± 0.86	31.11 ± 1.08
- Clay	65.62 ± 1.27	66.42 ± 1.00	66.64 ± 0.93	68.43 ± 1.21
Bulk Density (g cm ⁻³)	1.07 ± 0.12	0.88 ± 0.05	1.06 ± 0.04	1.00 ± 0.04
Soil pH (H ₂ O 1 : 5)	4.82 ± 0.11	4.26 ± 0.07	4.12 ± 0.04	4.42 ± 0.15
Δ pOH NaF ¹⁵	3.08 ± 0.05	3.29 ± 0.04	3.46 ± 0.05	4.21 ± 0.01
Organic C (g C kg ⁻¹)	55.72 ± 2.14	64.73 ± 1.88	63.94 ± 0.54	66.27 ± 0.75
Total N (g N kg ⁻¹)	3.97 ± 0.47	4.13 ± 0.15	4.31 ± 0.13	4.59 ± 0.09
CEC (cmol kg ⁻¹)	37.39 ± 3.68	34.21 ± 1.65	33.58 ± 4.56	35.91 ± 1.49
Fe _D ³⁾ (g kg ⁻¹)	4.94 ± 0.40	9.19 ± 0.10	5.54 ± 0.49	13.61 ± 0.23
Fe _O ⁴⁾ (g kg ⁻¹)	1.59 ± 0.12	2.91 ± 0.13	2.29 ± 0.43	3.64 ± 0.35
Al _O ⁵⁾ (g kg ⁻¹)	0.95 ± 0.08	1.50 ± 0.14	1.19 ± 0.06	2.29 ± 0.15

¹⁾ Standard deviation of mean (n=3)

²⁾ Soil reactivity

³⁾ Dithionite-extractable iron

⁴⁾ Oxalate-extractable iron

⁵⁾ Oxalate-extractable aluminum

Table 1: Characteristics of different ages of raised-bed soils

High clay content in the raised-bed soils affects other soil properties, such as bulk density. Bulk density of these soils ranged from 0.89 g cm⁻³ to 1.07 g cm⁻³ (Table 1). The highest soil pH was observed at the raised-bed soil of 27 years (Table 1). The high pH of this raised-bed soil is thought to be caused by the leaching of Al and Fe that might be a source of acidity in these soils. This is supported by the contents of Al and Fe in the raised-bed soil of 27 years was relatively lower than those in other raised-bed soils (Table 1).

3.2. The sorption of phosphate in response to fly ash application

Phosphate sorption isotherms of the raised-bed soils on tidal swamplands with different ages could be very well modelled using the Langmuir equation with r^2 values ranging between 0.91 and 0.98 (Table 2). The maximum capacity of the raised bed soils without fly ash application to absorb phosphate (Q_{max}) decreased with increasing the age of the raised-bed soils. The 3-year raised-bed soil without fly ash application had a Q_{max} value of 2424 mg P kg⁻¹ soil, and then the value decreased to 1787 mg P

kg⁻¹ soil on the raised-bed of 27-year (Table 1). The results of this study indicate that the maximum sorption of P on the raised-bed soils is determined by the age of the raised-bed soils.

Age of Raised-Bed (years)	Amounts of Added Fly Ash (Mg ha ⁻¹)	Q_{\max} (mg g ⁻¹)	k (L mg ⁻¹)	r^2
3	0	2424.40 ± 262.49	0.038 ± 0.0095	0.97
	25	2571.72 ± 147.12	0.028 ± 0.0074	0.91
9	0	2175.97 ± 52.48	0.022 ± 0.0021	0.98
	25	2421.68 ± 72.46	0.019 ± 0.0010	0.93
16	0	1824.71 ± 27.99	0.020 ± 0.0010	0.97
	25	2003.64 ± 27.37	0.018 ± 0.0010	0.96
27	0	1787.49 ± 114.34	0.025 ± 0.0050	0.95
	25	1883.08 ± 70.92	0.016 ± 0.0112	0.93

Table 2: Maximum sorption capacity (Q_{\max}) and binding affinity (k) derived from the Langmuir isotherm for phosphate sorption of raised-bed soils experiencing different ages with and without fly ash application. Numbers in parenthesis are standard deviation of mean (n=3).

The maximum sorption capacity of phosphate by the raised bed soils in this study was lower than the results of research on P sorption in mineral soils. The maximum sorption capacity of P in acid sulphate soils amended with fishpond sediment, fishpond water, and goat manure is 5000 mg P kg⁻¹ [22]. By considering the maximum phosphate sorption capacity in this study, a portion of the P fertilizer added to the raised-bed soils will be stabilized by soil minerals through a sorption mechanism so that P derived from fertilizer could not be used by plants. A number of geophysical-chemical properties of the soils play an important role in determining the capacity of phosphate sorption on the soils, such as the contents of iron- and aluminium-oxides [23,24], type of phyllosilicate clays [25,26]. Multivalent exchange cations such as Ca²⁺ and Mg²⁺ may function as a bridge (cation bridging) between the surface of clay minerals and phosphate negative charges [27,28]. Clay content is often reported as one of the soil characteristics affects the maximum sorption of phosphate in soils [29,30].

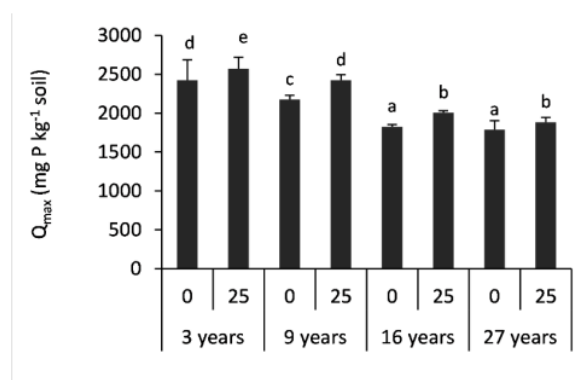


Figure 1. Changes in the maximum adsorption capacity (Q_{\max}) of raised-bed soils experiencing different ages in response to the application of fly ash. Vertical line above the bar is the standard deviation of mean (n=3). Similar letters on each bar show no statistical difference between with and without fly ash application for each raised-bed soil based on the LSD test at $P < 0.05$.

Results of variance analysis revealed that the maximum sorption capacity (Q_{max}) of phosphate in the raised-bed soils is influenced by the addition of fly ash. The maximum sorption capacity increased significantly ($P < 0.05$) at all raised bed soils with fly ash application. Results of this study indicate that the application of fly ash in the raised-bed soils may reduce P losses through the leaching process. The presence of Fe and Al oxides from fly ash in the soils is a major factor in determining the capacity of phosphate sorption in the soils. Fly ash is recognized as a material that has a large capacity to adsorb phosphate; therefore, fly ash is frequently used for phosphate removal from waste water [31,32]. The amounts of Fe extracted had a significant relationship with the concentration of phosphate removed from aqueous solution [33].

3.3. Desorption of phosphate in response to fly ash application

Results of the study showed that the amount of desorbed P increased with increasing the age of raised-bed soils. On the 3 year of raised bed soil without the application of fly ash, the proportion of P desorbed P was 4.4% of the adsorbed P and increased to 7.4% of the P adsorbed on the 27 year of raised bed soil (Table 3). Result of this study indicates the amount of desorbed P is controlled by a number of soil properties of raised-bed soils.

Age of Raised-Bed (Years)	Amount of Added Fly Ash (Mg ha ⁻¹)	Sorption (mg g ⁻¹)	Desorption (mg g ⁻¹)	% Desorption
3	0	1914.52	84.23	4.41 b
	25	1652.40	59.85	3.62 a
9	0	1630.97	83.59	5.13 c
	25	1481.54	54.70	3.69 a
16	0	1628.34	99.04	6.08 d
	25	1709.61	89.30	5.23 c
27	0	1551.76	114.31	7.41 e
	25	1386.95	70.92	5.17 c

Table 3: Sorption of phosphate, desorption of phosphate, and % of desorption of phosphate for raised bed soils experiencing different ages with and without fly ash application. Similar letters in the column of % phosphate desorption indicate no statistical difference between with and without fly ash application for each raised-bed soil based on the LSD test at $P < 0.05$.

Result of variance analysis showed that the application of fly ash influenced significantly ($P < 0.05$) the amounts of desorbed P from soil mineral-fly ash associations. The application of fly ash to the raised-bed soils decreased the proportion of desorbed P from soils (Table 3). This decrease is related to the stronger interaction between P ions and soil minerals in the presence of fly ash. Several studies showed that the presence of fly ash reduced leaching of phosphate ions from sandy soil [34] and acid soils [35]. Fly-ash generally contains a large amounts of Al³⁺ and Fe³⁺ cations [15,36], which may function as a bridge between the negative charges of soil minerals and P ions. A number of studies reported that the Fe and Al content in the soils (extracted with citrate-bicarbonate and ammonium oxalate) determines the strength of P adsorption in soils [37, 38, 39, 40]. From the perspective of phosphorous fertilization, results of this study imply that the application of fly ash to the raised-bed soils is able to increase the bond strength between phosphate ions and soil minerals so that a large number of phosphate ions from fertilizers would remain retained in the soils.

4. Conclusion

The results of study showed that the maximum capacity of soils to adsorb phosphate (Q_{max}) on the raised-bed soils of tidal swamplands varies according to the age of the raised-bed soils. The Q_{max} values of phosphate sorption decreases with increasing the age of raised-bed soils. The addition of fly ash increases the ability of raised-bed soils in adsorbing phosphate. The increase in Q_{max} value in the

raised-bed soils by the addition of fly ash is related to the contents of materials in fly ash such as Fe and Al oxides and other multivalence cations that function as bridging between soil minerals and orthophosphate ions. The amount of desorbed phosphate is also affected by the age of raised-bed soils, in which older raised-bed soils results in increases in the amount of desorbed phosphate. The application of fly ash to the raised-bed soils turns reduces the proportion of P desorbed from the associations of soil minerals–fly ash. This reduction is attributed to the improvement of bonding strength between orthophosphate ions and soil minerals by the presence of multivalent cation derived from the fly ash. The implication of this research is that the addition of fly ash to the raised-bed soils may increase the efficiency of phosphate fertilization on the raised-bed soils.

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