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Changes in soil phosphorus availability and nutrient uptake by maize following the application of wastewater-acidulated phosphate rock

A Niswati[1,5], A D Fajrianto[2], Sunyoto[3], K F Hidayat[3], S Yusnaini[1] and A A Rivaie[1]

[1]Department of Soil Science, University of Lampung, Jl. Sumantri Brojonegoro No.1 Bandarlampung 35145, Indonesia
[2]Department of Agrotechnology, University of Lampung, Jl. Sumantri Brojonegoro No.1 Bandarlampung 35145, Indonesia
[3]Department of Agronomy and Horticulture, University of Lampung, Jl. Sumantri Brojonegoro No.1 Bandarlampung 35145, Indonesia
[4]Assessment Institute for Agricultural Technology DKI Jakarta, Jl. Ragunan No. 32 Pasar Minggu, Jakarta Selatan 12520, Indonesia
[5]Corresponding author: ainin.niswati@fp.unila.ac.id

Abstract. The use of agro-industrial wastewater can reduce environmental pollution and emissions of greenhouse gases into the atmosphere. One of them is by utilizing its acidity to dissolve phosphate rock (PR) which is used for P fertilizer. The purpose of this study was to determine the effect of agro-industrial wastewater and PR dosage for P availability and nutrient uptake by corn in ultisol soil. Split plot design was arranged with wastewater of tapioca and tofu as a main factor and dosage of PR after acidulation as a sub-plot. The results showed that wastewater had no effect on the available soil P, soil pH, N uptake, P uptake, and dry weights of corn plants, but PR dosage had a significant effect on available soil P, N uptake. There is an interaction between agro-industrial wastewater and PR dosage on the P availability. For acidulation with tofu wastewater, the PR dosage used is lower for the same soil P availability compared to tapioca wastewater. At high P dosages, acidulation PR with wastewater does not have a significant effect on soil P availability. Phosphorus and nitrogen uptake by corn increased with the application of 950 kg ha^{-1} acidulated PR.

1. Introduction

Agro-industrial wastewater often becomes a problem if it is not handled and utilized properly, because it emits greenhouse gases like N_2O and CH_4 [1]. To overcome the environmental impact of agro-industrial wastewater is to utilize it to minimize environmental pollution and mitigate greenhouse gases to the atmosphere. Agro-industrial wastewater has the potential to dissolve phosphate rock allowing it to be more easily absorbed by plants [2]. Several agro-industrial wastewaters have acidic properties that could accelerate the solubility of phosphate rock (PR) utilized by wastewaters as a by-product of industrial treatments of tapioca and wastewater from tofu production. Besides, wastewater has a low pH, and may release some organic acids produced by microorganisms [3]. Wastewater of tofu or tapioca production has the possibility to increase the solubility of phosphorus in the soil such as an analogy with the use of manure which can increase the soil P availability [4]

Phosphorus (P), a crucial element for a plant, is essential to plant growth. Plants in highly weathered tropical soils are frequently severely P limited [5]. The main problem of this P nutrient is that it has a very low availability in the soil, due to the fixation by P absorbent elements such as Al3 $^{+}$, $Fe^{2+,}$ and Mn^{2+} [6]. The low availability of P is also due to the slow release nature of natural phosphorus rocks [7]. Natural phosphorus rocks can naturally be applied directly to the soil with a composition of Ca_3 $(PO_4)_2$. Natural phosphorus generally dissolves in water under acidic conditions. The availability of P fertilizer that is produced by the factory can dissolve because it had been previously oxidized so that the factory-made fertilizer can dissolve quickly.

Acidulation is the process of adding a strong acid reagent (solvent) containing H^+ ions with high concentrations that can replace Ca^{2+} ions that bind P elements in phosphorus rocks so that P elements are free and dissolved in water [8]. This is necessary because PR has a low solubility. The addition of conventional acid in acidulation will have an impact on high production costs. Therefore an alternative is needed to reduce the production costs. One alternative that can be used is tofu and tapioca agro-industrial wastewater which has acidic properties [2] and available in large quantities in Indonesia.

To sustain productive crops, especially maize, P fertilizers are applied in soils at varying dosages or concentrations for their efficiency. Meanwhile, plants require P which is often a limiting factor for growth and yield. Enhancing the availability of soil inorganic P to plant uptake is an important research subject. Reactive phosphates rock can provide a less expensive alternative to manufacture P fertilizers but they are only slowly soluble in most soils. To increase the soluble P from PR, it is essential to use acid agro-industrial wastewater before application to the soil as an alternative to solving the problem of P deficiency in the soil.

Phosphate rock fertilizers after acidulating by tofu or tapioca wastewater product have not been widely applied and tested in the field. Therefore, it is necessary to investigate and study their impact on soil and plant growth. The objective of the study was to determine the effect of tofu and tapioca wastewater acidulated with phosphate rock on soil available P, soil pH, N and P uptake, dry shoot biomass, and grain yield of maize (*Zea mays* L.).

2. Materials and methods

2.1. Site and material description

The study was carried out in ultisols soil in Research Station of Assessment Institute for Agricultural Technology of Lampung Province located at 135 m above sea level. This study was conducted during the dry season from June to October 2017.

The site of the experiment have a low pH where H_20 was 5.21 and soil available P was 2.01 mg kg^{-1}. The soil was classified as sandy clay loam texture (54% sand, 15% silt, and 31% clay). Phosphate rock from Egypt used for experiment has pH-H_2O 7.72 (electrometri), total P-25.09% (HCl 25%), and soluble P-6.08% (citric acid). The wastewater of tofu production had the following characteristic: pH-3.76; Chemical Oxygen Demand (COD)-9,900 mg L^{-1}, Biological Oxygen Demand (BOD)-925 mg L^{-1}; total P-0.00054%; total N-0.07% and for the wastewater of tapioca: pH-4.27; COD-10,525 mg L^{-1}; BOD-743 mg L^{-1}; total P-0.0008%; total N-0.03%.

2.2. Phosphate rock acidulation

One part of PR was submerged with two-part of wastewater of tofu or tapioca and incubated for 7 days. Every day the mix of wastewater and PR was stirred manually. After incubation, the PR was dried and crushed until has passed the 1 mm sieve and ready for treatment.

2.3. Experimental treatments

The research was conducted in a split-plot design with the type of wastewater (tapioca and tofu) as a main factor and the dosage of PR (control, 500 kg ha^{-1} RP unacidulated, 350 kg ha^{-1} acidulated PR, 500 kg ha^{-1} acidulated PR, 650 kg ha^{-1} acidulated PR, 800 kg ha^{-1} acidulated PR, and 950 kg ha^{-1} acidulated PR as a secondary factor. The environmental design was arranged in a randomized block design with three replications. So that there was 2 × 7 × 3 = 42 plots were built. The plots were 3 m × 4 m with maize plant in 75 cm × 25 cm planting distance. Maize plants were maintained as a standard role and were applied by nitrogen (urea 400 kg ha^{-1}) and potassium (KCl 200 kg ha^{-1}) as a base fertilizer according to the recommended dosages. PR treatment was applied during soil tillage and soil tidying, three days before plantation.

2.4. Field sampling and analysis
The sample collection for nutrient uptake was conducted in the vegetative maximum stage of the maize plant. Shoot biomass was cut from the base of the stem on the soil surface. Dry weights of shoots were recorded after 48h drying at 70 °C in an oven. Shoot biomass was ground to powder for nitrogen and phosphorus content analysis. Nutrient uptake was taken by conversion of dry shoot biomass with N and P content of maize. Nitrogen and phosphorus content in maize shoot were analyzed by Kjehdal and wet ashing method, respectively. Soil samples were taken by composite role from each plot for analysis pH (electrometri methods) and available P (Bray I). Maize grain yield were sampled from five plants for every plot in harvest time, dried, shelled, weighed, and converted to an area of hectares.

2.5. Statistical analysis
Data were analyzed by a two-way split-plot analysis of variance (ANOVA)-procedure and Least Significance Different (LSD) test with agroindustrial wastewater as the main factors and dosages of acidulated PR as secondary factors were used. For statistical analysis Excel software was used.

3. Results and discussion
Agricultural wastewater treatments do not show a significant affect on available P, soil pH, N uptake, P uptake, maize shoot biomass, and maize grain yield. However, the dosage of acidulated PR has a significant effect on available soil P, N uptake, P uptake, and maize grain yields, but no significant effect on soil pH and shoot biomass. Moreover, there was no interaction effect between agricultural wastewater and dosage of PR on all of the observation variables, except on soil available P (Table 1).

3.1. Available soil P
There was an interaction effect of PR dosage on available soil P. When PR was acidulated by tofu wastewater, the acidulated PR significantly increased the available soil P starting from a lower dosage of 350 kg ha^{-1} (P_2) acidulated PR. In addition, the original PR 500 kg ha^{-1} was significantly lower than tofu-acidulated PR on all treatment, except for some outliers of data in P_5. If PR was acidulated by tapioca wastewater, it had a different trend where acidulated PR increased the available soil P from the dosage of 500 kg ha^{-1} (P_3) (Table 2). This indicated that tofu and tapioca wastewater have different abilities to dissolve P [2]. On all dosage of acidulated PR, wastewater used to solubilizing PR was not significantly different between tofu and tapioca wastewater, except in dosage of 800 kg ha^{-1} acidulated PR in which the application of tapioca wastewater for acidulation PR was significantly higher than tofu wastewater. This is presumably due to the different properties of the wastewater applied, where the pH, COD, BOD, and the possibility of microorganisms living in the wastewater of tapioca and tofu are also different. The higher P availability in tapioca wastewater might also be due to the large number of microorganisms that are active there [9]. Until now, the references on this matter are still very limited. The acidity of an organic solvent will affect the solubility of P and the available soil P increases [10].

3.2. N and P uptake by maize
Figure 1 (A) shows that there were no significant difference of acidulated PR from of all dosage for maize N uptake, except for the highest dosage of acidulate PR 950 kg ha^{-1} where it shows a significant difference with both unacidulated PR 500 kg ha^{-1} and control. This is presumably due to higher solubility of P which facilitates the maize N uptake [11].

Table 1. Effect of dosages of wastewater-acidulated phosphate rock on soil available-P, soil pH, N and P uptake, maize dry biomass, and grain yields.

Acidulated PR	Soil available-P (g kg^{-1})	Soil pH (H_2O)	N uptake (kg ha^{-1})	P uptake (kg ha^{-1})	Shoot biomass (g plant^{-1})	Grain yields (g plant^{-1})
T_1P_0	3.59	4.38	27.90	5.58	30.97	71.70
T_1P_1	4.61	4.52	29.14	5.60	31.07	84.98
T_1P_2	6.39	4.56	42.39	7.79	40.81	135.84
T_1P_3	6.19	4.77	33.04	5.96	32.13	107.06
T_1P_4	6.50	5.16	43.48	7.76	41.86	136.84
T_1P_5	5.70	4.96	33.41	5.82	31.37	133.47
T_1P_6	7.08	5.17	47.96	9.15	46.64	143.38
T_2P_0	2.59	4.43	20.66	4.36	23.48	151.49
T_2P_1	4.48	4.71	21.48	4.66	24.41	157.63
T_2P_2	5.56	4.70	25.02	5.35	27.29	158.87
T_2P_3	5.76	4.69	26.89	5.53	28.19	162.35
T_2P_4	6.33	4.75	27.81	5.72	29.16	168.89
T_2P_5	7.93	4.85	30.56	6.14	30.51	170.51
T_2P_6	7.71	4.95	32.49	6.88	32.43	173.32
ANOVA F-test						
Wastewater (T)	4.90^{ns}	0.22^{ns}	1.4^{ns}	0,7^{ns}	1.02^{ns}	5.79^{ns}
Dosage of PR (P)	**24.05***	1.28^{ns}	**3.11***	**3.16***	2.12^{ns}	**8.36***
T × P	**3.38***	0.39^{ns}	0.17^{ns}	0.75^{ns}	0,71^{ns}	0.04^{ns}

Note. * indicates a significant difference at the $p \leq 0.05$ and ns not significantly different according to a two-way ANOVA with wastewater and dosage of RP as factors. T_1= acidulated tofu wastewater and T_2= acidulated tapioca wastewater. P_0= control (no P), P_1= 500 kg ha^{-1} (PR unacidulated), P_2= 350 kg ha^{-1} PR, P_3= 500 kg ha^{-1} PR, P_4= 650 kg ha^{-1} PR, P_5= 800 kg ha^{-1} PR, and P_6= 950 kg ha^{-1} PR.

Tabel 2. Interaction effect of wastewater-acidulated phosphate rock and kind of wastewater on soil available-P.

	Dosage of wastewater-acidulated phosphate rock						
Wastewater	P_0	P_1	P_2	P_3	P_4	P_5	P_6
	.... available P (mg kg^{-1})						
Tofu (T_1)	3.59 a (A)	4.61 ab (A)	6.39 cd (A)	6.19 cd (A)	6.50 cd (A)	5.70 bc (A)	7.08 d (A)
Tapioca (T_2)	2.59 a (A)	4.48 b (A)	5.56 bc (A)	5.76 cd (A)	6.33 c (A)	7.93 d (B)	7.71 d (A)
LSD 5%				1.23			

Note. Data followed by the same letter are not significantly different by LSD test (p<0.05). Small letter was read horizontal and capital letter was read vertical. T_1: acidulated tofu wastewater and T_2: acidulated tapioca wastewater. P_0: control (no P), P_1: 500 kg ha^{-1} (PR unacidulated), P_2: 350 kg ha^{-1} PR, P_3: 500 kg ha^{-1} PR, P_4: 650 kg ha^{-1} PR, P_5: 800 kg ha^{-1} PR, and P_6: 950 kg ha^{-1} PR.

Slightly different from P uptake, the increasing dosage of acidulated PR was not significantly different from the increasing P uptake of maize compared to control (without P fertilizer) (Figure 1, B), except for the highest dosage of acidulated PR 950 kg ha^{-1} (P_6) where it was significantly higher than control (P_0). This phenomenon indicates that the higher the P dissolves in the soil, the higher the P nutrient uptake [12].

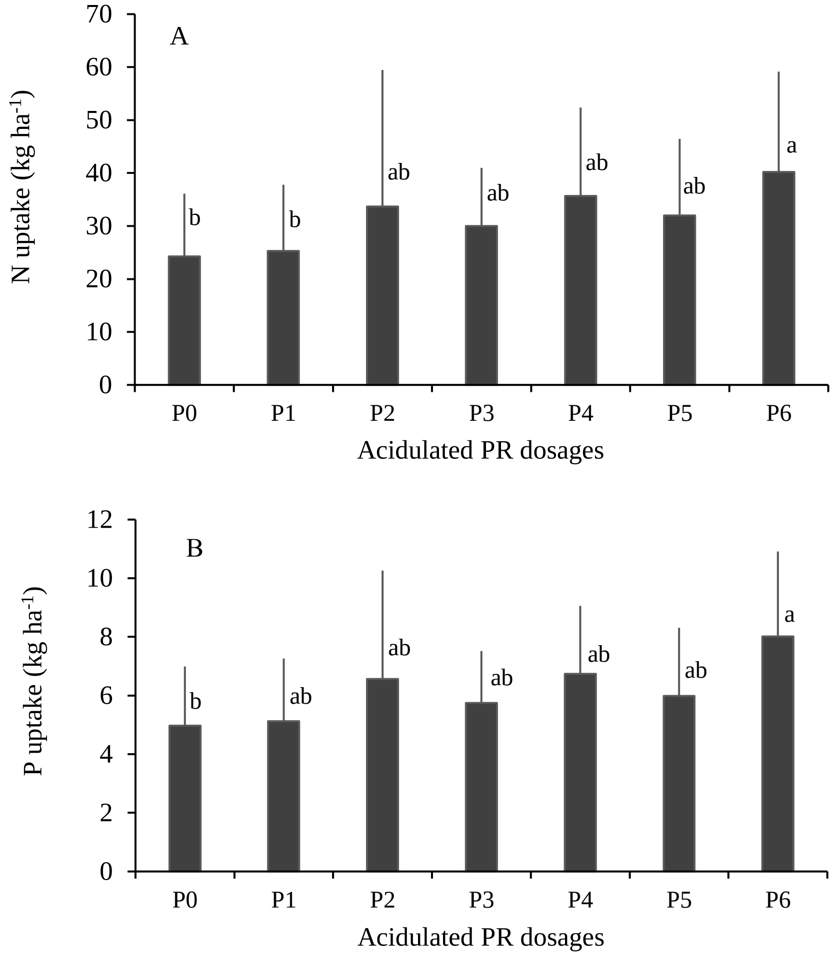

Figure 1. Changes in N and P uptake by maize following the application of different dosage of acidulated PR.
Note. P_0: control (no P), P_1: 500 kg ha^{-1} (unacidulation PR), P_2: 350 kg ha^{-1} PR, P_3: 500 kg ha^{-1} PR, P_4: 650 kg ha^{-1} PR, P_5: 800 kg ha^{-1} PR, and P_6: 950 kg ha^{-1} PR. The stick above the bar indicates the standard deviation from three replicates. Bar followed by the same letter are not significantly different by LSD test ($p<0.05$).

3.3. Maize grain yield

There were interaction effect of dosage PR on maize grain yield. When PR was acidulated by tofu wastewater, the increasing dosage of acidulated PR was significantly increased the maize grain yield starting from the lower dosage of 350 kg ha^{-1} (P_2). The maize grain yield increased more than 80% compared to control (P_0) or about 50% compared with non-acidulated PR dosage of 500 kg ha^{-1} (P_1). This result is thought to be due to the increased availability of P in the soil and this is in line with the research of Vanlauw et al [13] which reported that high P nutrient status increased maize grain yields. While, if PR was acidulated by tapioca wastewater, it had a different trend where acidulated PR did not significantly increase the maize grain yield (Table 3). With regard to the dosage of acidulated PR, tapioca wastewater used to solubilize PR was significantly higher for almost all dosage than tofu wastewater. This indicates that tapioca wastewater is better at solubilizing phosphate in increasing the maize grain yield. So far, there have been no reports on the use of this treatment, but the difference in the higher nutrient content in tapioca wastewater compared to tofu can confirm this [14]. Furthermore, besides tapioca wastewater have a low pH, it also contains large amount of total solid, such as carbohydrate, glucose, and total nitrogen [15].

Tabel 3. Interaction effect of wastewater-acidulated phosphate rock and kind of wastewater on the grain yield of maize.

Wastewater	Dosage of wastewater-acidulated phosphate rock						
	P_0	P_1	P_2	P_3	P_4	P_5	P_6
	.... Grain yield (g plant^{-1})						
Tofu (T_1)	72 a (A)	85 a (A)	136 c (A)	107 b (A)	137 c (A)	133 c (A)	143 c (A)
Tapioca (T_2)	151 a (B)	158 a (B)	159 a (A)	162 a (B)	169 a (A)	171 a (B)	173 a (B)
LSD 5%				25.3			

Note. Data followed by the same letter are not significantly different by LSD test ($p<0.05$). Small letter was read horizontal and capital letter was read vertical.

4. Conclusions

Application of tapioca and tofu wastewater for phosphorus acidulation in phosphate rock can be used as an alternative in increasing the solubility of phosphate rock fertilizer before it is applied in the maize plantation in the field because it may increase the avaibillity of soil phosphate. Nutrient uptake will increase if acidulated phosphate rock were applied with high dosages. Tapioca wastewater is better than tofu wastewater in increasing the maize production via acidulation PR. Tofu and tapioca wastewater can be used as an alternative to dissolve phosphate rock with cheaper price and simultaneously it will reduce environmental pollution.

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