Research Article
Inhibition of Phosphorus Adsorption to Goethite and Acid Soil by Organic Matter

Ahmad Kurnain

Department of Soil Science, Faculty of Agiculture, University of Lambung Mangkurat, Jalan A. Yani km 36, 70714 Banjarbaru, South Kalimantan, Indonesia

Abstract

Background: Most highly weathered soils in the tropics contain high concentration of (hydroxide) minerals, which are responsible for phosphorus adsorbed and consequently not available for plants. In practical manner Phosphorus (P) adsorption on acid mineral soils is commonly inhibited through addition of organic matters. **Materials and Methods:** For understanding the importance of organic matter addition on reducing P adsorption, this study was conducted to measure P adsorption on goethite as affected by humic acids and compare the result with P adsorption on acid mineral soil. Phosphorus adsorption to the goethite was studied by a bath method. A serie of phosphorus solution of 0.1-0.75 mM phosphorus and 0.1 and 0.3 g L^{-1} humic acids was added to 1 g L^{-1} goethite suspension in background electrolyte of 0.01 M $NaNO_3$ in which its pH was adjusted to certain range of pH with adding acid or alkaline solution. **Results:** In the absence of humic acids P adsorption to goethite was more pH-dependent than in the presence of humic acids. **Conclusion:** This implies that there is a change in charging behaviour of goethite due to the concomitant or previous adsorption of humic acid on goethite. Humic acid reduces P adsorption on goethite much more pronounced at pH<6, suggesting that in the normal pH, humic acid is very important to make phosphate more available for plants. The result was consistent with increasing P adsorption on acid soil from the top soil layer previously leached by rainfall.

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Corresponding Author: Ahmad Kurnain, Faculty of Agriculture, University of Lambung Mangkurat, Jalan A. Yani km 36, 70714 Banjarbaru, South Kalimantan, Indonesia Tel/Fax: +62 511 4772254

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In tropical regions with high annual rainfalls and temperatures soil parent materials were highly weathered and mostly generating acid soils. These soils are characterized by low soil fertility which is closely related to their poor chemical properties. The most important chemical properties of these acid soils are generally low soil pH, low bioavailability of phosphorus (P) and high concentration of iron and aluminum (hydroxides). The low bioavailability of P in acid mineral soils is caused by the fact that most of P, naturally present or added as fertilizer, are immobilized by soil solid fractions being either adsorbed or precipitated[1-4].

Iron and aluminum (hydroxides) are the most important minerals responsible for the P adsorption[3,5,6], because of their positively charged spesific surface and consequently high affinity for P. The most important minerals found in the tropical soils are kaolinite and sesquioxide minerals like goethite, hematite and gibbsite. In highly weathered soils, goethite is the solid phase expected finally in soils since it is the most thermodinamically stable of the iron (hydroxides)[7]. Crystal structure of goethite is characterized by three Fe^{3+} ions in hexagonal coordination with each O^{2-} and OH^- leading[8] to $Fe_3OH\text{-}OFe_3$. Positive charges of goethite are related to protonation of singly and triply coordinated O^{2-} with Fe^{3+} forming OH and OH_2 ligands. This implies that the charging behaviour of goethite will be determined[9] by pH. In common ranges of soil pH, surface charge of goethite will be positive, as the pH in which its point of zero charge (PZC) is more than 8.

The problem of low P bioavailability can be solved by return of organic materials to soils[10]. Incorporation of soil organic materials into soils can reduce P adsorption in acidic mineral soils[11]. Most studies showed that the presence of organic matter reduces P adsorption capacity of highly weathered soils possibly due to the result of competition for sorption sites between P and organic ligands[3-6,12-15]. However, the degree to which P become adsorbed on soils is not only governed by one or a combination of chemical and mineralogical properties, but also suffered by drastic reductions in soil organic matter due to soil erosion and inappropriate land uses thereby making P prediction in soils in the presence of organic matter inconsistent in most tropical soils with high rainfalls.

The aims of this study were to investigate P adsorption characteristics on synthetic goethite in the absence and presence of humic acids. The results were compared to field study of P adsorbed by acidic soils in which their top soil layers were intensively leached by rainfalls. Both studies were conducted to get an insight into roles of soil organic matters on P adsorption on acid mineral soil.

MATERIALS AND METHODS

Goethite was prepared according to procedure given by Hiemstra *et al.*[16]. A freshly prepared solution of 1 kg $Fe(NO_3)_3$ $9H_2O$ in 5 L bidest was slowly titrated (10 mL min^{-1}) with 2.5 M NaOH to a pH of 12. Goethite was kept in suspension in bidest at concentration of 47.7 g L^{-1}. For working suspension the goethite was diluted to 10 g L^{-1}. The BET surface area of the goethite is 99.9 m^2 g^{-1} as was determined with N_2 adsorption. Humic acids were prepared on the basis of their solubility in acid and alkaline solution. Humic acids were isolated from peat layer of forest floor taken from the selectively logged peat forest of central Kalimantan, Indonesia. Solid phase of humic acids obtained after two sequential extractions was purified with 0.6 M HF and 0.2 M HCl and then dissolved with bidest and following dialyzed againts bidest until the EC value was down to 5 µS cm^{-1}. Humic acid was freeze-dried and then dissolved with bidest to the concentration of 1 g L^{-1} at pH 4 for working solution. The total organic C of the HA was 40.4%.

In order to characterize P adsorption on goethite in the absence and presence of Humic Acids (HA), an experiment was performed at different amounts of working P solution and 1 g L^{-1} goethite over a wide range of pH in a background electrolyte of 0.01 M $NaNO_3$. Amounts of HA added were 0.0, 0.1 and 0.3 g L^{-1}. The experiment was carried out in plastic tubes with a total volume of 40 mL. For adjusting pH certain amounts of 0.064 M HNO_3 or 0.117 M NaOH were added. Tubes were shaken in an end-over-end shaker for 3 days. After shaking the suspensions were centrifuged at 16500 rpm for 30 min. Supernatants were collected for measuring P concentration colorimetrically. The remaining supernatants in tubes were used for determining equilibrium pH. Adsorption isotherms were built by interpolation from series of P concentration edges. The P adsorption isotherms in the absence of HA were fitted to Langmuir, two surface Langmuir and Langmuir-Freundlich equations. The best one would be used to fit both P adsorption on goethite in the presence of HA and soil P adsorption on acid mineral soil. Fitting data with the equations was conducted by interation using Excel-Solver menu based on least square difference.

The second study was conducted to determine P adsorption capacity of an acid mineral soil that was previously treated by constructing three organic wastebaskets with

Table 1: Parameters of some adsorption isotherm equations of phosphorus to goethite at different pH in the absence and presence of humic acids (0.1 and 0.3 g L^{-1} HA)

	pH 4	pH 6	pH 7	pH 4+0.1 HA	pH 6+0.1 HA	pH 7+0.1 HA	pH 4+0.3 HA	pH 6+0.3 HA
Langmuir								
Q max (μmol m^{-2})	2.53	2.25	2.06					
K	5.38	3.33	4.20					
R^2	0.94	0.93	0.75					
Two surface Langmuir								
Q_1 max (μmol m^{-2})	0.58	0.52	0.48					
Q_2 max (μmol m^{-2})	1.95	1.73	1.60					
log K_1	7.64	7.64	7.64					
K_2	3.83	2.23	2.51					
R^2	0.95	0.94	0.77					
Langmuir-Freundlich								
Q max (μmol m^{-2})	2.79	2.66	2.68	2.98	3.19	3.31	3.18	3.13
K	192.91	32.95	5.37	1.64	0.16	0.08	0.11	0.19
m	0.22	0.21	0.21	0.24	0.25	0.26	0.25	0.25
R^2	0.97	0.99	0.94	0.92	0.98	0.98	0.92	0.93

dimension $75 \times 75 \times 75$ cm^3 so that its top soil layer was more intensively leached by rainfalls. Soil samples for determining P adsorption isotherm were collected on the top soil layer 10-20 cm at the beginning and subsequently after 4 months of construction of the organic waste basket at three different sites. As control, three non-organic waste baskets were also made at three different sites. Each 5 g of air-dried soil sample was subjected to addition of different amounts of P working solution that consists of 0, 4, 8, 20, 40, 60 and 100 mg L^{-1} P with a background electrolite of 0.01 M $CaCl_2$. The experiment was carried out in plastic tubes with a total volume of 50 mL. Tubes were shaken in an end-over-end shaker for 3 days. After shaking the suspensions were sifted through Whatman paper No. 41. Supernatants were collected for measuring P concentration colorimetrically. The remaining supernatants in tubes were used for determining equilibrium pH. Phosphorus adsorption was calculated from the difference between the initial and the equilibrium P solution concentrations in the batch experiment. Based on the result of the first experiment P adsorption isotherms were fitted to Langmuir-Freundlich equation. Fitting data with the equation was conducted by interation using Excel-Solver menu based on least square difference.

RESULTS AND DISCUSSION

Characteristics of P adsorption on the synthetic goethite in the absence and presence of humic acids are shown in Table 1. All adsorption equations have good ability to characterizing P adsorption on the goethite. In the absence of humic acids three adsorption equations resulted in a similar trend of P adsorption parameters in term of increasing pH. With increasing pH capacity and affinity of the goethite for

P adsorption decreased. This implies that P adsorption on the goethite in the absence of humic acids is significantly pH-dependent[17]. Effects of pH on P adsorption on (hydroxides) including goethite could be explained by charging behavior of the mineral (hydroxides)[8,18,19]. Hiemstra and Van Riemsdijk[18] assumed that charging of goethite is related to protonation of rows of singly coordinated FeOH(H) and triply coordinated $Fe_3O(H)$ surface groups. This evidence is in line with Elsheikh *et al.*[20] that P adsorption on allophane was reduced with increasing pH and thus charging of allophane surface is pH-dependence due to (HO)Al(OH_2) groups can either protonate or deprotonate depending on the pH of solution. At higher pH, allophane will be negative charge and otherwise[21] at lower pH.

Compared with the other equations, the Langmuir-Freundlich equation has better fit to P adsorption data. The Langmuir equation was originally developed for monocomponent adsorption and consequently it is not suitable to characterize a multicomponent of P and humic acid adsorption using the simple Langmuir equation[2]. Accordingly the LF equatuion was used to fit P adsorption in the presence of humic acids, as shown in Table 1. In the presence of humic acids P adsorption on the goethite is less pH-dependent. Phosphous adsorption on mineral (hydroxides) is not only determined by the charging behaviour of adsorption sites, but also affected by existence of organic molecules[6,10,11,22]. As a macro molecule humic acids occupied adsorption sites of goethite and consequently inhibited the charging of goethite[23].

Figure 1 shows P adsorption isotherm on the goethite in the absence and presence of humic acids at pH 4 (Fig. 1a), pH 6 (Fig. 1b) and pH 7 (Fig. 1c). The effect of humic acids on the amount of P adsorbed appears to be much more
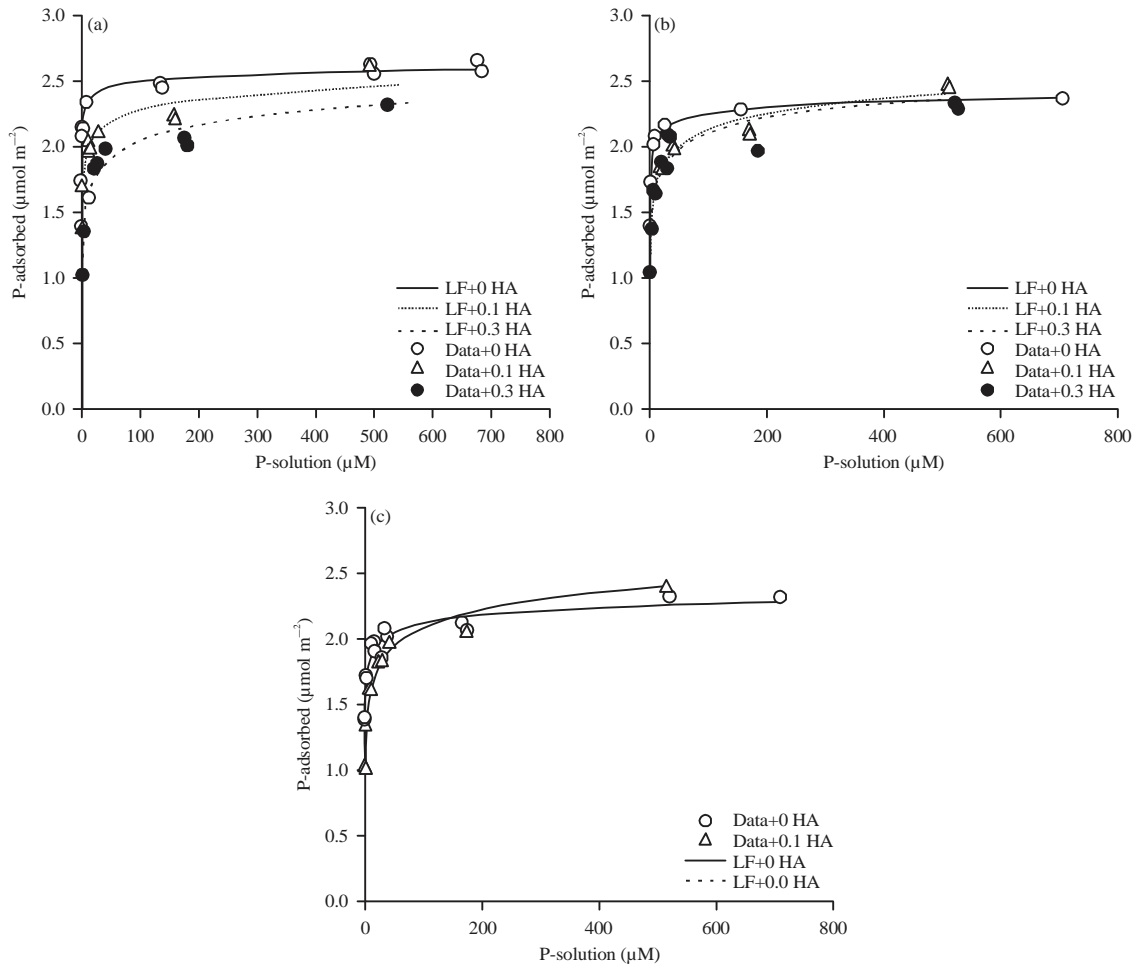
Fig. 1(a-c): Phosphorus adsorption to goethite in the absence and presence of humic acids (0.1 and 0.3 g L^{-1}) at (a) pH 4, (b) pH 6 and (c) pH 7, as described using the Langmuir-Freundlich equation

pronounced at pH<6, suggesting that in the normal pH of soils addition of organic materials is very important to P more available for crops. This also implies that competitive ability of humic acids on adsorptive sites decreases when the pH>6. This can be understood by considering that carboxyl groups are predominant for interaction with metal (hydroxides) as was stated by Kaiser *et al.*[24]. The carboxyl groups of humic substances would fully be deprotonated at pH close[7] to 7. Therefore, it is likely that the carboxyl groups of humic acids compete with phosphate for adsorption sites.

The adsorption isotherm of phosphorus in the absence and presence of humic acids can be described with the Langmuir-Freundlich equation. At the beginning, the slope is very steep indicating possibly an electrostatic character, followed by a pseudo plateau at elevated equilibrium concentration. This also implies high affinity of the goethite for P. Table 1 shows the average affinity (K) decreases with increasing pH, that might be due to a progressive increase in

the singly coordinated surface groups of FeOH$^{-1/2}$ and the triply coordinated surface groups[18] of Fe$_3$O$^{-1/2}$. In the presence of humic acids the average affinity decreases at a given pH as the humic acids-coated goethite is less positive charge.

It is generally recognized that anion adsorption on (hydroxide) surfaces involves ligand exchange with H$_2$O and OH$^-$ being displaced[25,26]. Kaiser *et al.*[24] observed that the DRIFT spectroscopy of dissolved organic matter and acidic humic substances adsorbed on the surface of Al and Fe (hydroxides) confirms the importance of carboxyl groups for the adsorption by ligand exchange. In terms of ligand exchange decrease in the extent of the adsorption with increasing pH can be explained firstly by decreasing in positive charge of surface groups as the surface is progressively deprotonated resulting in the decrease of adsorption capacity (Q$_{max}$) and secondly by increasing electrostatic repulsion[6] due
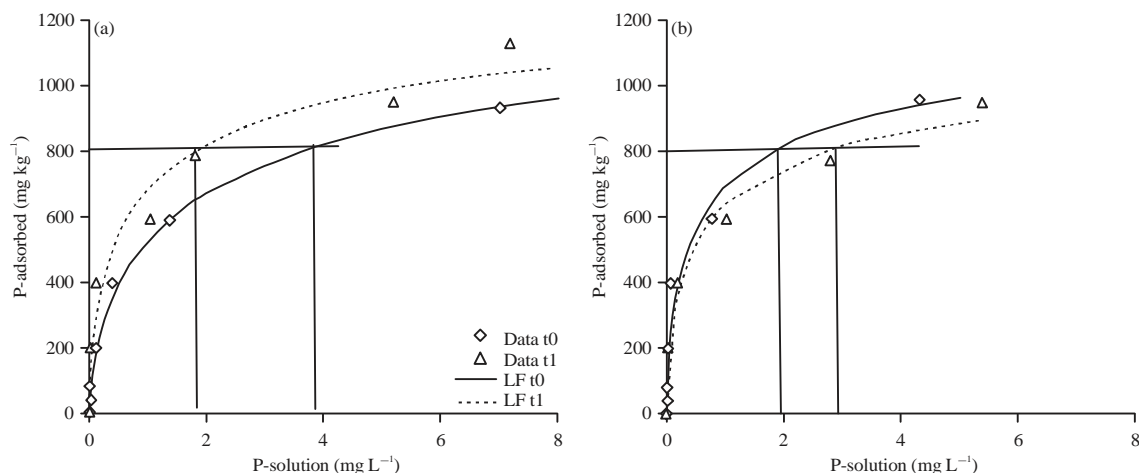
Fig. 2(a-b): Phosphorus adsorption on the top soil layer of acid mineral soil (a) Without addition of organi matters and (b) With addition of organic matters, before (t0) and after 4 months (t1) intensively leached by rainfalls as described using the Langmuir-Freundlich equation

to a progressive increase in surface of $Fe-OH^{-1/2}$ and $Fe-O^{-3/2}$ so that the average affinity (K) decreases (Table 1). However, decrease in the adsorption with increasing pH is still questioned, because the extent of adsorption should be also be taken account for charging behaviour of adsorptive ions.

It is necessary to point out that electrostatic character of P adsorption on goethite is reduced with adsorbed humic acids, as can be interpreted from the parameter of m which increases. This is very clear that the Langmuir isotherm can only be used very well if there is not many electrostatic forces responsible for ion adsorption. Since the phosphorus-humic acids-goethite system will at least give a promising model for describing P adsorption in soils in the presence of soil organic matters.

Figure 2 shows P adsorption isotherm on the top soil layer of acidic mineral soils without (Fig. 2a) and with (Fig. 2b) addition of organic materials those were intensively leached by rainfalls. Adsorption data has a good fit with the LF equation. As leaching intensively, P adsorption capacity on the top soil layer of acidic soils changed depending on the addition of organic materials. Without the addition of organic materials, the P adsorption capacity increased and P bioavailability in soil solution decreased, as showed at before and after intensively leaching for 4 months (Fig. 2a). On the contrary with the addition of organic materials the P adsorption capacity decreased and P-available in soil solution increased (Fig. 2b). The adsorption capacity of P on acidic soils ranged between 800-1200 mg kg^{-1} that is comparable to obtained by Moazed *et al.*[27]. The result was approximately 10 times lower than the P adsorption capacity of the goethite that is equivalent to 8000-10000 mg kg^{-1}. This comparison is lower than that was measured on temperate soils in which their P adsorption capacity reached approximately 200 mg kg^{-1} and consequently the comparison being 40-50 times[28]. This may imply that role of (hydroxide) minerals is of importance for adsoprtion sites of tropical acidic soils. The result also implies an importance of soil organic layers on increased P bioavailability for crops on acidic mineral soils. As showed by Onweremadu[29] that presence of organic matters reduces P sorption capacity of oxisols and ultisols.

CONCLUSION

Humic acids and phosphorus can interact with each other for adsorption sites of the goethite. In the presence of humic acids the P adsorption decreased in which was effectively occured at pH less than 6. Comparison of the laboratory result with the field study of P adsorption in the absence and presence of orgnic matters gave a valueable information of the importance of soil organic matters on increased P-bioavailability for crops. Results of the present study revealed an importance of added soil organic matters inhibiting subsequent P adsorption on acidic mineral soils.

ACKNOWLEDGMENTS

SIGNIFICANT STATEMENTS

- The present study is of importance to give a scientific consideration on organic material addition that may be applied to overcome low bioavailability of phosphorus in acidic soils
- The present study implies that effectiveness of organic material addition in order to reduce P-adsorption depends on environmental soil pH

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