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Effect of Humic Acid and Molybdate on Phosphate Adsorption in Typic Hapludult of Cigudeg, Bogor

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ABSTRACT

Humic acids containing carboxyl and hydroxyl groups that have the ability to cover the P adsorption site in Typic Hapludults. Molybdate has similarity behaviour with phosphate in theacid soils. Research aim was to study the effects of molybdate and humic acid to the kinetics of phosphate adsorption in Typic Hapludults of Cigudeg, Bogor. Important of kinetics is to get accuration of materials transport, to control influence on anion mobility, that the assessment is needed for the efficient application of Mo and P. Aplication humic acid and molybdate as competitor anion of phosphate was conducted with combination of humic acid and Mo concentration as double anions. Many models describe the kinetics for the adsorption of phosphate by soils i.e. zero order, first order, second order, and Elovich. As ststistically, there was not interaction of humic acid and molybdate on P adsorption. Application of humic acid with rate of 100 mg.L^{-1} was not effective decrease P adsorption in Typic Hapludults. It was due to the pH of the adsorption system that get near to its pKa of carboxyl gruop about 5. Meanwhile aplication 2 and 5 mmol.L^{-1} of molybdate significantly decrease of P adsorption. The second order kinetics models apropriate to the adsorptionof P in the Typic Hapludults of Cigudeg, with determination coefficients value (R^2) of 0.999-1 and standard error value (SE) of 0.001–0.011.The results suggest that the molybdate as competitor anion affected the kinetics for the adsorption of phosphate due to the charge of molybdate.

Keywords: Humic Acid, Kinetics Models, Molybdate, P Adsorption, Second Order

INTRODUCTION

In the development of agricultural commodities in acid soils will face various technical problems such as low level of soil fertility and water availability in the dry season for dry land. Some of the characteristics of acid soils include the nature of acid soil reactions (low pH) associated with high Al content, high P fixation, low exchangeable base content, iron and manganese content close to the toxic limit of plants, and low availability of micro nutrients. Adsorption of molybdate in the soil is positively correlated with concentrations of Fe and Al oxides are particularly prone to Mo deficiency (Mengel *et al*., 2001). The characteristics that become obstacles in the management of acid soilcan be overcome by fertilizing technology, liming, and management of organic materials. Addition of humic acid can increase the availability of P, able

to reduce the solubility of Al and Fe on acid soils (Ifansyah, 2013).

Phosphorus (P) is one of most needed nutrient by plant, major essential plant elements. It have function as a component of certain enzymes and proteins, adenosine triphosphate (ATP), ribonucleic acids (RNA), deoxyribonucleic acids (DNA), and phytin. Where ATP is involved in various energy transfer reactions, and RNA and DNA are components of genetic information (Jones, 2012). Meanwhile as essential element, Molybdenum (Mo) have important role in the biogeochemical cycle of nitrogen (N). It have functions in plant as a component of two major enzyme systems, nitrogenase and nitrate reductase, nitrogenase being involved in the conversion of nitrate (NO_3) to ammonium (NH_4). The requirement for Mo is reduced greatly if the primary form of nitrogen (N) available to the plant is NH_4 (Jones, 2012).

Molybdate has similarity behaviour with phosphate or sulphate in the soil. Adsorption of molybdate by sequioxides and clay minerals has analogous way to phosphate. Highly weathered soils, like Ultisols and Oxisols containing large amount of amorphous and crystalline Fe oxide minerals. Where adsorption of molybdate is affected by concentrations of Fe and Al oxides (Mengel *et al.*, 2001). Thus, P and Mo deficiencies often occur in highly weathered acid soils (Vistoso *et al.*, 2009). Soil adsorption properties can cause nutrient deficiencies in the soil, that can be avoided by proper fertilization of dose and time of application. It is therefore important to know the adsorption kinetics of nutrient in the soil.

The need for kinetics is to know accurately both the accumulation and transportation of materials (Sparks, 2012), to control influence on anion mobility, transport, and bioavailability (Vistoso *et al.*, 2009), that the assessment is needed for the efficient application of Mo and P fertilizers. Many models describe the kinetics for the adsorptionof phosphate by soils i.e. zero order, first order, second order, Elovichwhich were described as Eqs (1), (3), (4), and (6) (Vistoso *et al.*, 2009); (Sparks, 2012); (Huang *et al.*, 2015). The zero order equation is expressed as follow equations:

$$q_t = q_0 - k_0 t \quad\text{...(1)}$$

Here q_t, and q_0 denote the quantity at time (t) and time zero, where k_0 is the rate constant of zero order sorption. The first order equation is generally expressed as follows:

$$\frac{dq_e}{dt} = k_1 (q_e - q_t) \quad\text{...(2)}$$

After integration and applying the boundary conditions, for q_t=0 at t=0 and $q_t = q_t$ at t=t, the integrated form of Eq. (2) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad\text{.........................(3)}$$

where q_e and q_t are the amounts of phosphates adsorbed at equilibrium and at time t, respectively, and k_1 is the rate constant of first order adsorption. If the rate of adsorption is a second order mechanism, the second order kinetic rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad\text{...(4)}$$

where k_2 is the rate constant of second order sorption and q_e is the amount of phosphates adsorbed at equilibrium. The Elovich equation is given as follows:

$$\frac{dq_t}{d_t} = \alpha e^{-\beta q_t} \quad\text{...(5)}$$

The integration of the rate equation with the same boundary conditions as the first and second order equations becomes the Elovich equation:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad\text{...(6)}$$

where α is the initial sorption rate, and the parameter β is related to the extent of surface coverage and activation energy for chemisorption. The aim of this research was to compare the effect of the persence of humic acid and molybdenum on the phosphate adsorption in acid soil.

MATERIALS AND METHODS

Typic Hapludults was taken from Cigudeg, Bogor district, province of Jawa Barat. Soil pH was measured in water using soil suspensions at a soil:solution ratio of 1:5. Organic carbon and humic carbon was measured with Walkley and Black titration method meanwhile total N with Kjeldahl method. Total and available phosphate were extracted with wet combustion HNO_3-$HClO_4$ and Bray 1, respectively and measured colourimetrically measured at 889 nm in a spectrophotometer. Total Mo was extracted with wet combustion HNO_3-$HClO_4$ and measured by AAS. Exchangeable base cations (Ca, Mg, K, Na) were extracted with 1 M NH_4Cl and analyzed using atomic absorption spectrophotometry (AAS) for Ca and Mg, flamephotometer for K and Na. Al-p and Fe-P measured by Chang and Jaction methods. Exchangeable aluminium was extracted with 1 M KCland analyzed by titrition. And the cation exchange capacity (CEC) was extracted with 1 M NH_4Cl, and measured by distillation process with Kjeldahl method (Balai Penelitian Tanah, 2009).

Humic acid was produced by mix a weighed amount of cow manure compost (pass a 2-mm sieve) with a 0.1 M solution of NaOH at a soil/solution ratio of 1:10 and shaked it continuously overnight (IHSS, no date). The supernatant, containing fulvic acid and humic acid, was separated from the precipitate as humin. Further, supernatant was acidified to pH 2.0 by adding drops of HCl to precipitate the humic acid fraction. The supernatant, containing fulvic acid, is then separated from the precipitate as humic acid (Tan, 2014).

Persence effect of humic substance and molybdenum to the adsorption kinetics of the soil to the phosphorus were obtained in batch systems using a soil:solution ratio of 1:20 with 0.1 M KCl as background electrolyte at an initial pH of 5.0. For the competitive adsorption

studies the initial humic substance concentrations were 0 and 100 mg.L^{-1} while molybdate ($Na_2MoO_4.2H_2O$) concentrations were 0, 2, and 5 mmol.L^{-1}as (Mo_0, Mo_2, and Mo_5), and each of these concentrations were tested with 0, 1 and 2 mmol.L^{-1} phosphate (K_2HPO_4) as (P_0, P_1, dan P_2) (Vistoso *et al.*, 2012). So there were 18 combination treatments of humic, phosphate, and molybdate i.e. P_0 Mo_2, H-P_0 Mo_2, and etc. Samples were weighed and placed in polypropylene tubes, and the suspensions were shaken in an end-over-end shaker for 2 h at ambient temperature. The soil suspensions were then filtered with Whatman 42, aliquots of the supernatants were taken for analysis. P was determined by the phosphomolybdate-ascorbic acid method (Sadzawka *et al.* 2006). The amount of anion sorbed was derived from the difference between the initial and final solution concentrations. The experimental data were statistically analyzed using SPSS 16 version for windows. Appropriate adsorption kinetic model was evaluated by the determination coefficient (R^2) and standard error (SE) of (Dong, 2016). The values of R^2 and SE were used to compare the applicability of the different models at a confidence level of 95%.

RESULT AND DISCUSSION

Chemical properties of experiment soil were shown in Table 1. Used soil has characteristics as acidic soil with pH 4.62. Soil has moderate C content about 2.23%, 0.0632% humic carbon, and total nitrogen was low (0.16%). So C/N ratio was 13.82 and categorized as moderate level. High total P concentrations about 274.15 mg.kg^{-1} P_2O_5, but with low availability of P about 3.73 mg.kg^{-1}, this is in accordance with the acidic soil reaction that cause the low availability of P. Futhermore high total Fe about 813.79 mg.kg^{-1} and total Al about 47 mg.kg^{-1} would decrease availability of P. Soil contain of 25.6 mg.kg^{-1} Al-P, 20.1 mg.kg^{-1} of Fe-P, and 3.8 mg.kg^{-1} of Mo. Soil cation exchange capacity (CEC) scored as moderate level, i.e. 16.85 cmol (+).kg^{-1} with very low base saturation value of 13.83. The soil was classified as Typic Hapludult (Badan Penelitian dan Pengembangan Pertanian, 2014); supported with the soil characteristics of clay texture, acidic reaction, moderate score CEC, and very low base saturation (USDA, 2014). The soil was red colour, high degree of soil development and high significant clay accumulation in the soil. It was detected the texture class of clay with 1.49% sand, 6.56% silt, and 91.95% clay (IUSS Working Group WRB, 2014).

Another identification of the soil was clay content

Table 1. Chemical properties of Cigudeg Typic Hapludult

Parameter	Unit	Value	Score*
Texture			
Sand	%	1.49	clay
Silt	%	6.56	
Clay	%	91.95	
pH (H_2O 1:5)		4.62	acidic
Total N	%	0.16	low
Org-C	%	1.65	moderate
C/N		13.82	moderate
BO	%	3.85	
P Bray 1	mg kg^{-1} (P_2O_5)	3.73	very low
P ($HClO_3$ & HNO_3)	mg kg^{-1} (P_2O_5)	274.15	
Base cations			
K	cmol (+) kg^{-1}	0.20	low
Na	cmol (+) kg^{-1}	0.17	low
Ca	cmol (+) kg^{-1}	1.12	very low
Mg	cmol (+) kg^{-1}	0.99	low
Al-dd	cmol (+) kg^{-1}	1.37	
CEC	cmol (+) kg^{-1}	16.86	moderate
Base Saturaion		13.82	very low
Al-P	mg kg^{-1}	25.26	
Fe-P	mg kg^{-1}	20.10	
Fe	mg kg^{-1}	813.79	
Al	mg kg^{-1}	47.00	
Humic-C	%	0.063	
Mo ($HClO_3$ & HNO_3)	mg kg^{-1}	3.8	

Remarks: ** Score was based on (Balai Penelitian Tanah, 2009), w/w = weight per weight.

identification by X-ray diffraction. Air dried treatment gave interlayer space about 7.3 Å that show metahalloysite clay minerals, 4.17 and 3.54 Å that show kaolinite clay minerals content. Heating with temperature of 550°C gave interlayer space about 2.7 Å that show collapse or dissapear of the peak as characteristics of kaolinite and matahalloysite minerals. Clay treatment with K saturation gave interlayer space about 7.4 Å as characteristics of the metahalloysite. Saturation of clay with Mg gave 7.19 Å space interlayer asa characteristic of kaolinite clay minerals. Saturation by a cation makes it possible to fill the existing cation vacancies and, by displacement of the exchangeable cations, to obtain homoionic samples that present uniform expansion of the layers of the expansible phyllosilicates (the quantities of interlayer water depend on the exchangeable cations) (Pansu and Gautheyrou, 2006). According to (Pansu and Gautheyrou, 2006); (Tan, 2011) and with that characteristics, the soil contain of kaolinite and metahalloysite as clay
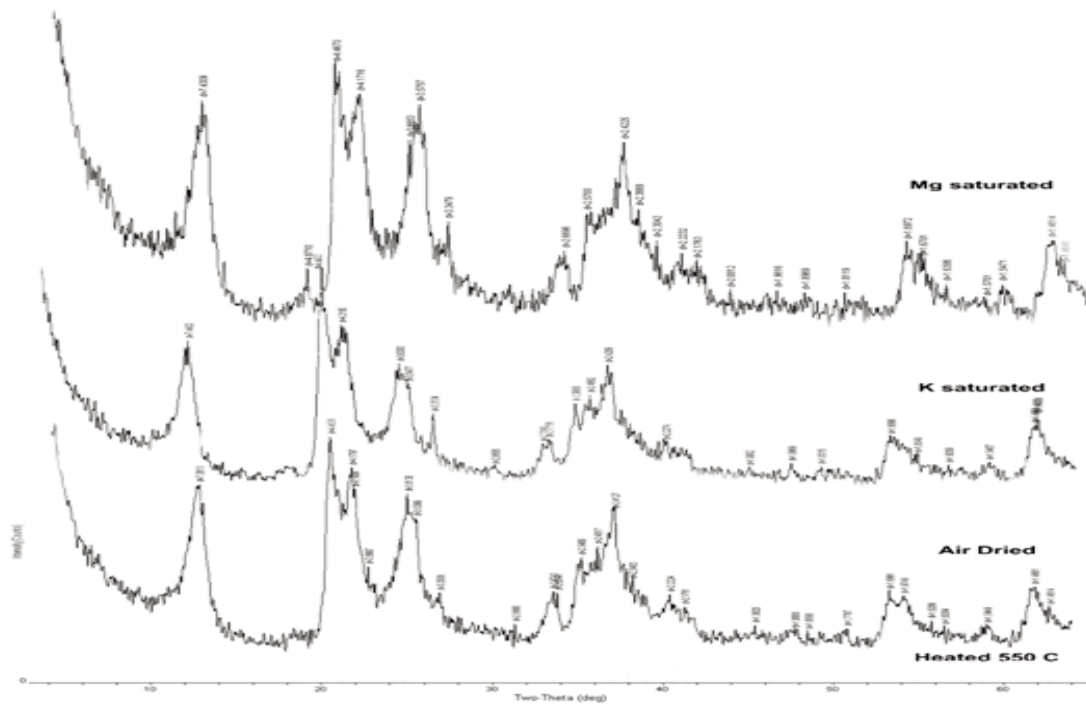
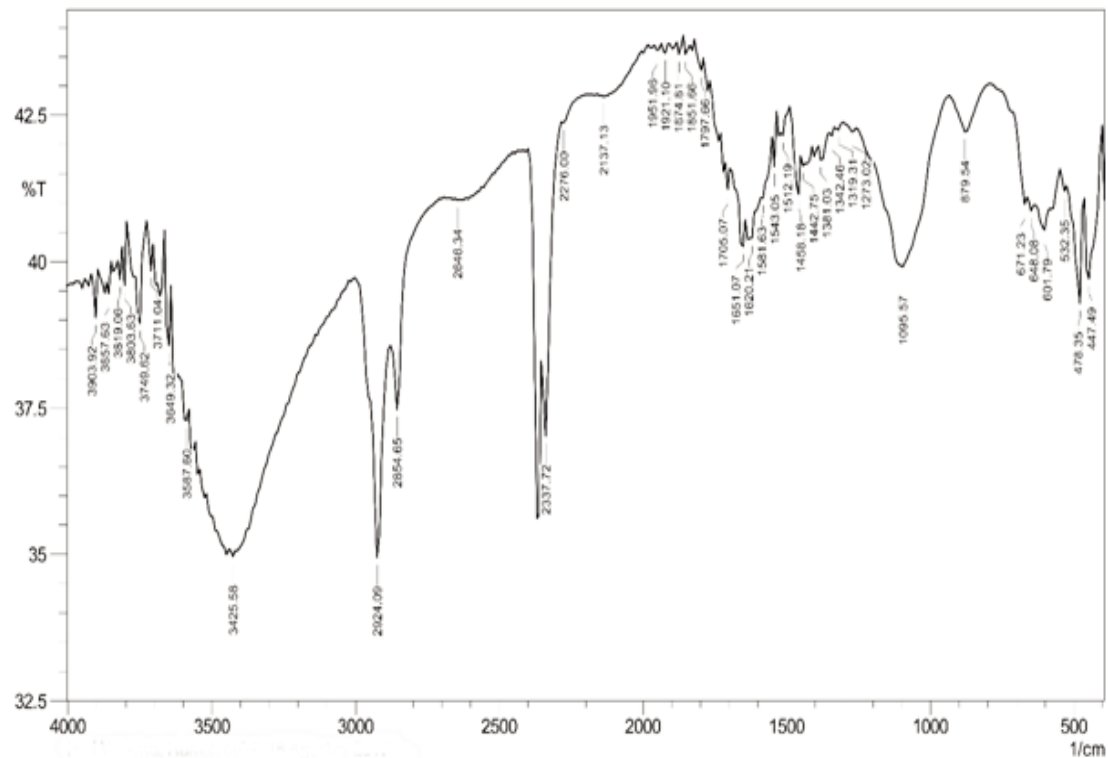**Figure 1.** X-ray diffraction of clay minerals of Cigudeg Typic Hapludult

Figure 2. FTIR analysis of humic acid extraced from cow manure compost

minerals. The soil also contain of gibbsite, geothite and hematite as oxides and hydroxides and feldspar as silicates minerals. In the most highly weathered soils in the tropics such as Ultisols and Oxisols contain high concentration of hydroxide minerals, which are responsible for phosphorus adsorption (Kurnain, 2016).

The extraced humic acid contain of 56.4% C.

Humic acid is usually rich in carbon, which ranges from 41% to 57% (Tan, 2011). Steelink (Steelink, 1985) showed carbon content in humic acid reached 53.8% to 58.7%. This indicates the occurrence of carbon fixation or retardation occurring during the synthesis of humic material and with the increased humidity rate. Decomposition of organic residues is generally characterized by the loss of C in the form

Table 2. Effect of humic acid to the P adsorption of Cigudeg Typic Hapludult with initial P of 1 mmol L^{-1}

Adsorption Time (minute)	Adsorbed P (mg kg-1) with initial P of 1 mmol L^{-1}								
	Mo of 0 mmol L^{-1}			Mo of 2 mmol L^{-1}			Mo of 5 mmol L^{-1}		
	Non-Humic	Humic	sig	Non-Humic	Humic	sig	Non-Humic	Humic	sig
20	90.2506	87.0229	0.443	84.7188	89.1385	0.256	84.2100	86.9400	0.366*)
40	92.6151	92.4557	0.715	90.3927	90.8693	0.590	87.7867	88.5133	0.505
60	93.3578	92.9096	0.534	91.2499	91.2646	0.954	88.8233	88.3967	0.637
80	93.8527	93.4855	0.503	91.6394	91.5810	0.737	89.3733	89.2600	0.854
100	93.9917	93.9709	0.940	92.2226	92.1876	0.854	89.9133	89.4833	0.413
120	93.9547	93.2440	0.377	92.5616	90.0085	0.344	89.8933	88.3967	0.442

Remarks: *) significant difference at sig ≤ .05

Table 3. Effect of humic acid to the P adsorption of Cigudeg Typic Hapludult with initial P of 2 mmol L^{-1}

Adsorption Time (minute)	Adsorbed P (mg kg-1) with initial P of 2 mmol L^{-1}								
	Mo of 0 mmol L^{-1}			Mo of 2 mmol L^{-1}			Mo of 5 mmol L^{-1}		
	Non-Humic	Humic	sig	Non-Humic	Humic	sig	Non-Humic	Humic	sig
20	167.58	166.74	0.923	161.11	160.59	0.925	159.28	159.08	0.909*)
40	169.90	176.00	0.339	167.05	171.75	0.058	164.57	164.02	0.936
60	176.32	178.29	0.326	171.55	172.64	0.507	167.47	164.70	0.729
80	178.26	179.73	0.512	173.99	170.46	0.256	164.35	162.46	0.726
100	180.11	180.52	0.743	175.12	175.18	0.960	168.90	168.67	0.968
120	178.27	179.46	0.782	175.44	171.48	0.240	168.30	169.85	0.751

Remarks: *) difference is significant at sig ≤ .05

Table 4. Effect of molybdate persence to the adsorption of phosphate by Typic Hapludult of Cigudeg, Bogor.

Concentration of Mo in soil solution (mmol L^{-1})	Adsorbed P with initial P 1 mmol L^{-1} in minute adsorption					
	20	40	60	80	100	120
0	90.2506 a	92.6151 a	93.3578 a	93.8527 a	93.9917 a	93.9547 a*)
2	84.7188 a	90.3932 b	91.2499 b	91.6394 b	92.2226 b	92.5615 b
5	84.2073 a	87.7886 c	88.819 c	89.3726 c	89.9112 c	89.8933 c

Remarks: *) Column values followed by the same letter are not significantly different according to Duncan's multiple range test (P = 0.05)

of CO$_2$. However, when humification occurs, some C will enter the humus and material humic. Nitrogen content in humic acid about 3.1% where the avverage nitrogen content in the soil humic acid were 2.6% to 5.05%. (Steelink, 1985); (Tan, 2014)). According to other research, humic acid was extracted from the soil of a citrus orchard (Rhodoxeralf) (Basra, Israel) had elemental composition C 53.4%; N 5.4%; O 35.6%; H 5.2%; S 0.4% (Chotzen *et al.*, 2016).

Identification of humic acid with Infrared spectroscopy, there were about 40 peak in the Infrared spectra of extraced humic acid. Figure 2 shows that lots of in hydroxyl and carboxylic groups exist in humic acid, according to (Zhenghua *et al.*, 2001) that were responsible for behavior adsorption. Strong absorption at 3,425 cm^{-1} show the O–H and N–H stretch, strong absorption at 2,924 cm^{-1} of C–H stretch and 2855 cm^{-1} of aliphatic C-H stretch, strong absorption at 1651 cm^{-1} of C=O stretch (amide I). There were not absorption in 1000 cm^{-1}, but were in 1095 cm^{-1} that show C–C, C–OH, C–O–C typical of glucosidic linkages, polymeric substances, and Si–O impurities in humic compounds. Humic acid exhibits a strong absorption for C–H vibrations at 2980 to 2920 cm^{-1} (Maccarthy and Rice, 1985); (Tan, 2011), and a stronger absorption for both carbonyl and carboxyl vibrations in COO– form at 1,720 and 1,650 cm^{-1}, respectively. Humic acid spectra have, in addition, no absorption bands at 1,000 cm^{-1} (Tan, 2011).

Strong P adsorption in acid soils such as Oxisols and Ultisols and in volcanic soils with andic properties is mainly caused by the presence of large hydrous Fe and Al surface areas in the soil (Rengel, 2003); (Anwar and Sudadi, 2013). The presence of a competitor, such as humic acid, reduces phosphate adsorption and reveals that both ions are in competition
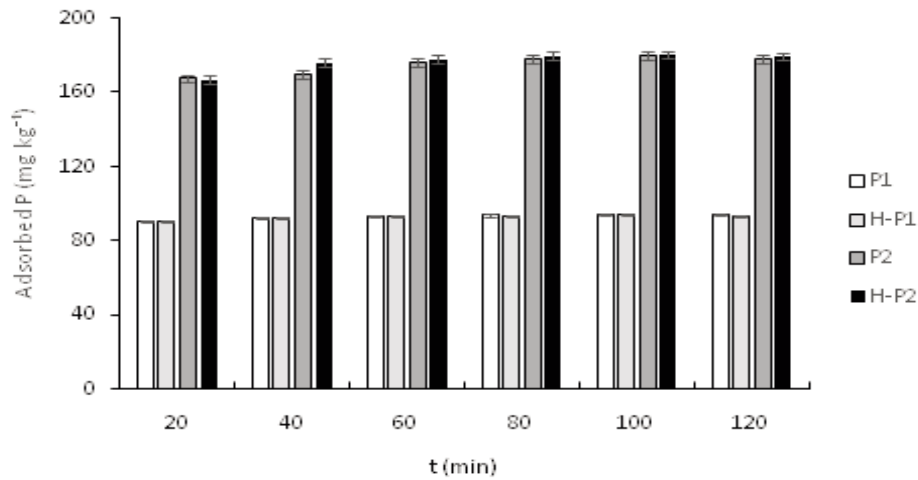
Figure 3. Effect humic acid substances aplication on the phosphate adsorptions in Typic Hapludult of Cigudeg. Bogor. P1 : initial P concentration of 1 mmol.L^{-1}; H-P1 : aplication Humic acid with initial P concentration of 1 mmol L^{-1}; P2 : initial P concentration of 2 mmol.L^{-1}; H-P2 : aplication Humic acid with initial P concentration of 2 mmol.L^{-1}
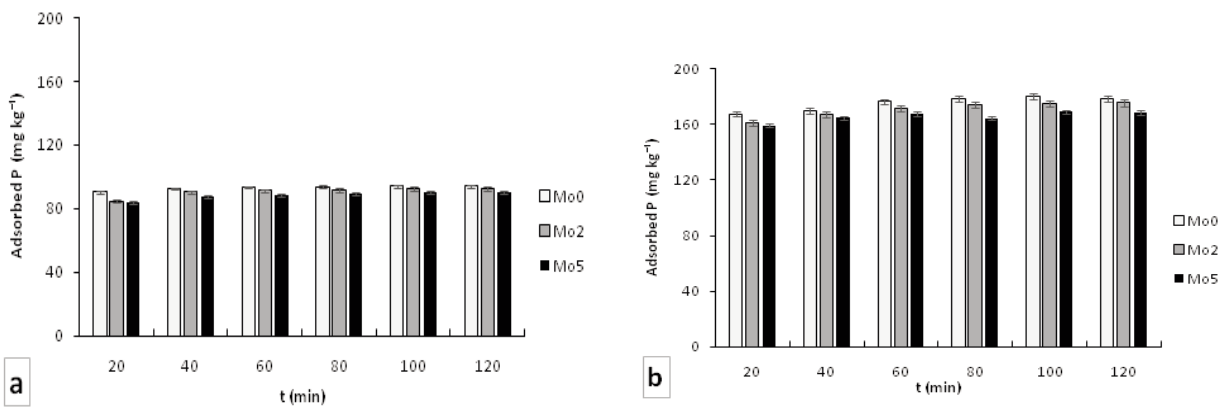

Figure 4. Effect of Molybdate persence on the phosphate adsorption in Typic Hapludult of Cigudeg. Bogor. Mo0 : absence of Molybdate; Mo2 : persences of Molybdate concentration of 2 mmol.L^{-1}; Mo5 : persences of Molybdate concentration of 5 mmol.L^{-1} . a) initial P of 1 mmol.L^{-1};b) initial P of 2 mmol.L^{-1}.

for surface sites (Perassi and Borgnino, 2014). Organic matter like humic acid can increasing soil pH and forming strong complexes to controls the activity of Al and Fe in soil solution. The lowered Al and Fe activities will decrease the chelate or precipitation of P with these ions to increase availability phosphor for the plant (Ifansyah, 2013). Soil humic acid (SHA) and PO$_4$ generated electrostatic field and competition for adsorption sites were responsible for the mechanism by which SHA inhibited adsorption of PO4 as much as 27.8% by goethite (Fu *et al*., 2013).

The adsorption of P as a function of time are presented in Figures 3 and 4. The adsorption of phosphate increased with time. Figure 3 showed two clearly steps A fast initial reaction, P was quickly sorbed of 90.25 ppm in 20 minute for about 95% from initial P concentrations 1 mmol.L^{-1} and 167 ppm about 88% from initial P concentrations 2 mmol.L^{-1}, followed by a slow adsorption (up to 24

h). It indicate the highly adsorption site in the soil. As independent, aplication of humic acid with rate of 100 mg.L^{-1} was not significantly affected to the adsorption of P. By T-test, there was not difference of P adsorption in the soil affected by humic acid at all time of adsorption in both initial P concentration (Table 2 and 3). Same case to the amorphous minerals, application of humic acid with rate of 100 mg.L^{-1}, was not effective in decreasing P adsorption (Hanudin *et al*., 2014). Addition of humic and fulvic acids does not always decrease P adsorption in soils (Ohno and Crannell, 1996). In volcanic soils, the new humic acid–Al complex formed by adsorption of humic acid acts as a new source of P adsorption sites (Rengel, 2003). Metal in the form of oxides or hydroxydes can make complex with organic groups in humic acid, that has capacity to hold phosphate ions (Weir and Soper, 1963). Some studies have showed that increasing the organic matter content of

Table 5. Effect of molybdate persence to the adsorption of phosphate by Typic Hapludult of Cigudeg, Bogor.

Concentration of Mo in soil solution (mmol L^{-1})	Adsorbed P with Initial P 2 mmol L^{-1} in minute adsorption					
	20	40	60	80	100	120
0	167.5754 a	169.8985 a	176.3176 a	178.2622 a	180.1076 a	178.2741 a*)
2	161.1088 a	167.0496 a	171.5469 ab	173.9901 a	175.1248 a	175.4432 ab
5	159.2844 a	164.5678 a	167.4739 b	164.3532 b	168.8995 b	168.3017 b

Remarks: *) Column values followed by the same letter are not significantly different according to Duncan's multiple range test (P = 0.05)

Table 6. Values of determination coefficient (R2) and standard error (SE) obtained from the model kinetic fitting to the experimental data for the adsorption of phosphate by Typic Hapludult of Cigudeg, Bogor.

Treatment	Zero Order		First Order		Second Order		Elovich	
	SE	R2	SE	R2	SE	R2	SE	R2
P1 Mo0	39.770	0.279	0.111	0.876	0.001	1.000	0.464	0.918
P1 Mo2	37.720	0.210	0.100	0.877	0.002	1.000	1.157	0.874
P1 Mo5	37.200	0.237	0.057	0.854	0.001	1.000	0.637	0.931
P2 Mo0	73.030	0.212	0.069	0.812	0.004	1.000	1.808	0.900
P2 Mo2	70.570	0.189	0.039	0.941	0.002	1.000	0.844	0.982
P2 Mo5	70.180	0.256	0.038	0.689	0.005	1.000	1.829	0.791
H-P1 Mo0	39.840	0.290	0.140	0.652	0.004	1.000	0.506	0.867
H-P1 Mo2	39.470	0.320	0.118	0.173	0.011	0.999	0.995	0.354
H-P1 Mo5	38.330	0.312	0.049	0.419	0.006	1.000	0.604	0.634
H-P2 Mo0	74.130	0.225	0.085	0.740	0.002	1.000	2.092	0.869
H-P2 Mo2	72.040	0.246	0.084	0.411	0.006	0.999	3.348	0.647
H-P2 Mo5	69.410	0.238	0.066	0.788	0.008	0.999	2.238	0.747

soil does not decrease adsorption of P, however, suggest that organic matter affects the binding energy of adsorbed P and possibly as a result of phosphate adsorption with little energy by cation bridges, therefore increase the availability of phosphate (Fiona R., Dean and James, 2010).

There is interaction of phosphorus with molybdenum in the soil that affects availability both of phosphorus or molybdenum (Kopsell, Kopsell and Hamlin, 2015). Phosphate strongly competed with molybdate (Roy, Hassett and Griffin, 1986) for adsorption siteson the Andisols, causing molybdate adsorption to decrease by 10−27% (Vistoso et al., 2012). The competition also was showed by (Sun and Selim, 2017) that amount of Mo sorbed decreased substantially with increasing P concentration, which indicates that P has a competitive effect for available adsorption sites. As independent, persence of Molybdate significantly affected to the adsorption of P (Table 4 and 5). Persence of molybdate 2 and 5 mmol.L^{-1} decrease P adsorption significantly in both initial P concentration of 1 and 2 mmol.L^{-1} about 1.5-8%. Higher concentration of Molybdate persence in the solution will reduceadsorbed P in the soil, suggesting strong competition between the two anions. At high concentrations phosphorus was more effective in

inhibiting molybdate adsorption (Vistoso et al., 2012), and ofcourse similarly thehigh concentrations molybdate was more effective in inhibiting phosphorus adsorption.

The adsorption of phosphate increased with time. Phosphate adsorption patern showed two steps as mentiones before, fast initial adsorption (up to 20 minutes), followed by a slow adsorption. The similar results were obtained by (Zeng et al., 2003); (Vistoso et al., 2009); (Vistoso et al., 2012) for the adsorption of phosphate by Andisols and for the adsorption of phosphate by on goethite (Luengo et al., 2006). Four different kinetics models using the least square regression analysis was tested to describe the adsorption of phosphate in the Typic Hapludult (Table 6). Accordance model determined by correlate the experimenral data with the linear models of the four models, respectively. Zero order kinetics models gave very low value of determination coefficients (R^2) in range 0.189-0.320 with high difference between experimental and theoretical adsorbed phosphates at equilibrium (SE) is very high between 37.20 and 74.13. The model and the experimental data show a bad fit. So the adsorption of phosphates onto Typic Hapludult is not ilustrated with zero order kinetics models. The first order kinetics model gave value of
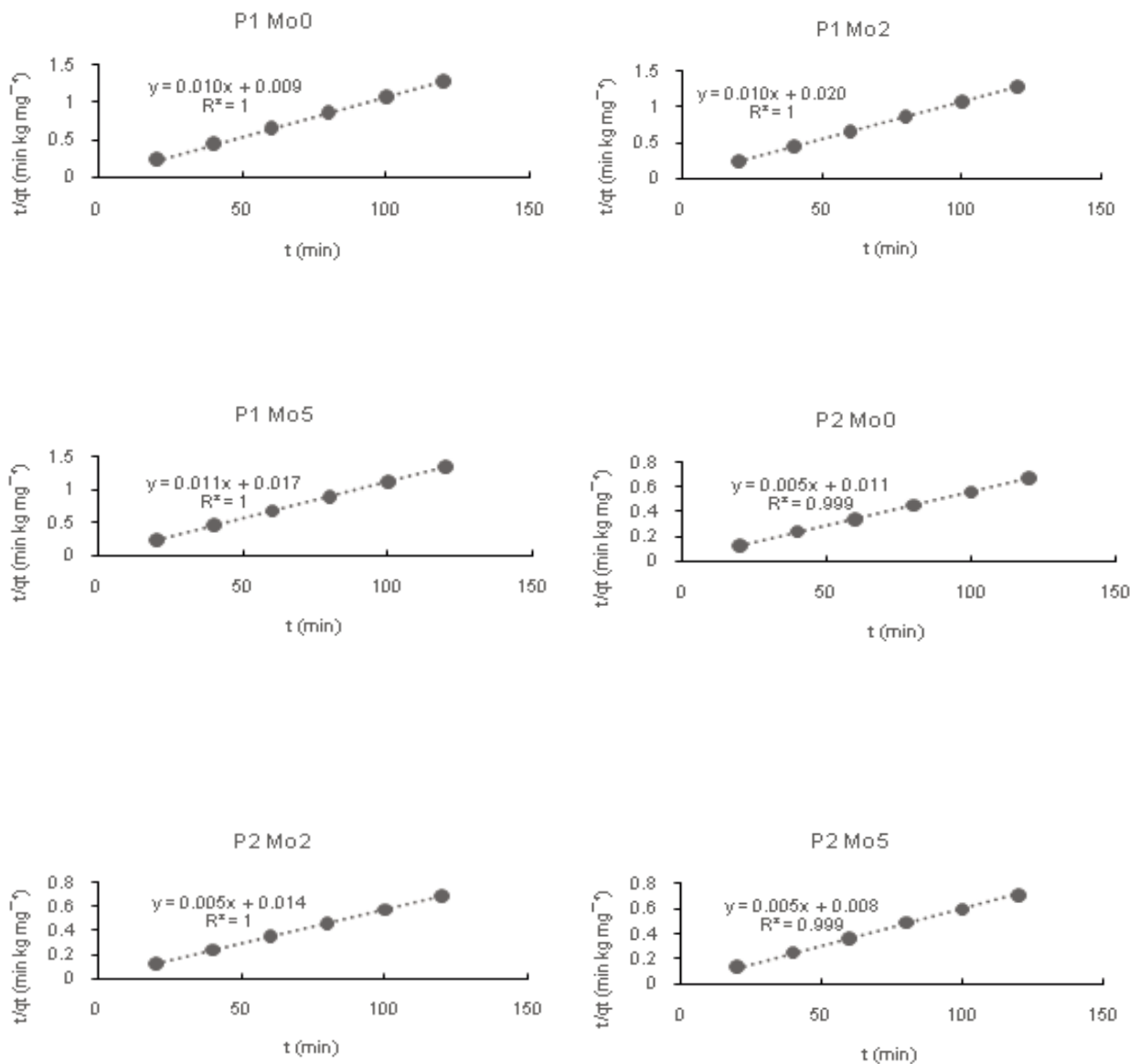
Figure 5. The second order plot for adsorption of P affected by Molybdate in Typic Hapludult of Cigudeg, Bogor.

correlation coefficients are relatively low lying between 0.411 and 0.941. Difference between experimental and theoretical adsorbed phosphate at equilibrium is very high about 0.055-0.199. These results also state a bad fit between the model and the experimental data. So the first order kinetics model is not ideal for adsorption of phosphates onto Typic Hapludult. For the second order kinetics model, the determination coefficients for all treatment are higher than 0.99 with value 0.999-1. The difference between the experimental and theoretical adsorbed phosphate at equilibrium is very small (less than 1%) with value of 0.001-0.011. Meanwhile Elovich kinetics model show variable range value of determination coefficients between 0.354 and 0.982. Difference between experimental and theoretical adsorbed phosphate at

equilibriumis very high about 0.506-3.348. From four kinetics models, the second order kinetics models apropriate to the adsorption P in the acid soil, according to (Otero *et al*., 2013) that second order kinetic model gave an appropriate description of PO_4-P adsorption onto estuarine sediments and onto the upstream agricultural soils. But was different to the (Vistoso *et al*., 2012); (Zeng *et al*., 2003) that found that the adsorption of phosphate could not be adequately described by a zero, first, or second order kinetic model.

The second order kinetics models parameters for the adsorption of phosphate are listed in Table 7. The second order kinetics models gave the best determination coefficients (R^2) value, both without and with humic acid treatment, close to perfect value of 1 with

Table 7. Values of the parameters (q_e and k_2) derived from fitting the experimental data for the adsorption of phosphate in Typic Hapludult of Cigudeg. Bogor to the second order kinetics model.

Treatment	$1/q_e$	q_e	$1/k_2q_e^2$	k_2
P1 Mo0	0.0105	94.8017	0.0099	0.0112
P1 Mo2	0.0106	94.0517	0.0207	0.0055
P1 Mo5	0.0110	91.1893	0.0175	0.0069
P2 Mo0	0.0055	182.4482	0.0117	0.0026
P2 Mo2	0.0056	179.3049	0.0143	0.0022
P2 Mo5	0.0059	170.2031	0.0085	0.0041
H-P1 Mo0	0.0106	94.1676	0.0077	0.0146
H-P1 Mo2	0.0110	90.9805	0.0005	-0.2416
H-P1 Mo5	0.0112	89.1521	0.0035	0.0359
H-P2 Mo0	0.0055	182.6555	0.0087	0.0034
H-P2 Mo2	0.0057	174.4862	0.0063	0.0052
H-P2 Mo5	0.0058	171.6136	0.0131	0.0026

low SE value. It was according to the (Huang *et al*., 2015) in phosphate adsorption by Zr/Al-Mt and (Zhang *et al*., 2015) that second order kinetic model more suitable for describing the adsorption behavior of phosphorus in soils. The amount of phosphates sorbed at equilibrium (qe) was affected by persence concentration of molybdate but not by the persence of humic acid in the soil solution. The equilibrium adsorption capacity (qe) increases as the higher initial phosphate concentration in the soil solution. Further, it was found that the variations value of the rate constant (k_2) that not affected by persence concentration of molybdate and the persence of humic acid in the soil solution.

CONCLUSION

Humic acid with contain of 54% C and 3.1% N, shows that lots of hydroxyl and carboxylic groups exist in humic acid, with strong absorption at 3425 cm^{-1}, 2,924 cm^{-1}, 2,855 cm^{-1}, 1651 cm^{-1} and no absorption in 1000 cm^{-1} in FTIR. As ststistically, application of humic acid with rate of 100 mg.L^{-1} was not effective in decreasing P adsorption in acid soil. Identification by X-ray diffraction of the soil show some characteristics, the soil contain of kaolinite and metahalloysite minerals, also contain of gibbsite, goethite and hematite as oxides and hydroxides and feldspar as silicates minerals. Mineral contents are according to the soil analysis i.e. acidic soil pH, low moderate CEC, and low base saturation.Meanwhile aplication 2 and 5 mmol.L^{-1} of molybdenum significantly affected P adsorption. The adsorption of phosphate increased with time. Phosphate adsorption patern showed two steps, fast initial adsorption (before 20 minutes), followed by a slow adsorption. The secondorder kinetics model gave determination coefficients (R^2) for all treatment with value 0.999-1. The difference between the experimental and theoretical (SE) adsorbed phosphate at equilibrium is very small (less than 1%) with value of 0.001-0.011. Meanwhile Elovich kinetics model show variable range value of determination coefficients (R^2) between 0.354 and 0.982. Difference between experimental and theoretical adsorbed phosphate at equilibrium (SE) is very high about 0.506-3.348. From four kinetics models, the second order kinetics models apropriate to the adsorption P in the Typic Hapludult of Cigudeg, Bogor.

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