Scientific Research Publishing

Mutual Adsorption of Lead and Phosphorus onto Selected Soil Clay Minerals

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Abstract

Mutual adsorption of lead (Pb) and phosphorus (P) at pH 5 onto three soil clays materials (kaolinite, montmorillonite, and allophane) was studied to know interaction of the anion and the cation at surface of the clays. Adsorption of Pb was determined on montmorillonite, kaolinite and allophane with the following pretreatments; 1) untreated clay (control), 2) phosphate treated clay (P-clay) and 3) clay pre-treated with both P and Pb (P-Pb-clay). Adsorption of P was determined on montmorillonite, kaolinite and allophane with the following pretreatments; 1) control 2) Pb treated clay (Pb-clay) and 3) P-Pb-clay. The adsorption of Pb on the untreated clays was in the order: montmorillonite > allophane > kaolinite. On allophane and kaolinite Pb adsorption was in the order P-clay > P-Pb-clay > control. For montmorillonite, the trend was: P-Pb-clay = control > P-clay. Phosphorus adsorption was in the order Pb-clay = P-Pb-clay > control for montmorillonite and kaolinite, Pb-clay > control > P-Pb-clay for allophane. The findings suggested that pre-treatment with phosphate increases Pb adsorption on kaolinite and allophane, and decrease on montmorillonite, while pretreatment with Pb increases phosphate sorption on all clays, and both Pb and P increased adsorption on montmorillonite and kaolinite and decrease on allophane.

Keywords

Allophane, Kaolinite, Montmorillonite, Mutual Adsorption, Lead and Phosphorus

1. Introduction

Heavy metals are among the major contaminants of the environment, with se-

rious effects on animal and human health [1]. Lead is among the most toxic heavy metals, even at low concentrations, to animals and human beings. Although Pb naturally occurs at low concentrations in the earth's crust, volcanic activity, weathering and erosion of the soil materials [2] and anthropogenic activities such as coal burning, mine tailings, metalmelting and emission from car-exhaust cause serious environmental pollution with Pb [2] [3]. Addition to this, although Pb is not toxic to plants, its accumulation in tissue of plants growing on polluted soil could have serious consequences on animal and human health. These effects depend on the availability of Pb in the soil, which is affected by adsorption and desorption of the metal on the surfaces of soil colloids.

Montmorillonite is one of the most abundant clay minerals in soils, especially those that are not highly weathered and is potential binding agent for pollutants as a result of its high specific surface area and cation exchange capacity [4] [5]. On the other hand, kaolinite is a clay mineral that is abundant in highly weathered soils like Ultisols and Oxisols, in association with oxides of iron (Fe) and aluminum (Al) [4] [5]. Allophane is a unique clay mineral that is abundant in weathered volcanic ash soils, and is a principal material of clay fraction in andisols and podzols. The wall structure of as nano-ball allophane has been proposed as aluminm-nesosilicate structure composed of curved gibbsite sheet with monomeric SiO_4 tetrahedral attached to it [6]. The surface activity of these colloids contributes in the adsorption and immobilization of contaminants in soil.

The interaction between toxic metals and clay mineral colloids is important in surface chemistry, soil science, and pollution studies [7] [8] [9]. For example, the interaction between phosphate and soil minerals affects the surface activity of the colloid and mobility of P in the soil. Hence, adsorption of heavy metals on soil minerals could be affected by the presence of phosphate ions in the soil system. Extensive studies have been conducted to investigate the possibility of using phosphate to reduce mobility and bioavailability of heavy metals in soils and clay materials [10] [11] [12]. Based on work by [13] and [14], the pretreatment of soils with phosphate is now a widely accepted technique to remediate soils and solid waste contaminated with Pb. Recently there have been studies conducted on the adsorption of Pb on kaolinite pretreated with phosphate [15] [16] [17]. However, there is a paucity of studies on mutual adsorption on Pb and phosphate on montmorillonite and allophane, which are among the most important colloids, is soils. Therefore, the objective of this study was to investigate the effect of mutual adsorption of Pb and phosphate by montmorillonite, kaolinite and allophane.

2. Material and Methods

2.1. Clay Minerals

Montmorillonite (JCSS-3101) and kaolinite (JCSS-1101) samples used in this study were supplied by the Clay Science Society of Japan. Na-montmorillonite and Na-kaolinite were prepared by saturating the clay samples with sodium

(Na). The clay samples were washed three times with 1M NaCl followed by washing with 80% methanol until Cl⁻ free and finally with acetone and air-dried. Pumice grains containing nano-ball allophane were collected from a volcanic ash soil from Kakino, Kumamoto prefecture, Japan. In order to obtain the pure nano-ball allophane, free from contaminants such as imogolite, volcanic glass, and opaline silica, only the inner portion of the pumice grains was used [18]. The fraction with less than 0.2 μm equivalent diameter was separated by centrifugation after ultrasonification at 28 kHz and dispersion at pH 10. The collected sample was flocculated by saturation NaCl solution and washed with water, then stored as suspension at pH 6 in 10 mM NaCl. The prepared allophane was subjected to X-ray diffractometry, infrared spectroscopy, and thermal analysis, and was proven to be free from contaminants. The Si/Al ratio of allophane used was determined by the acid oxalate method [19] as 0.99, and contents of the other metals except for Na were negligible. The allophane was the high Si/Al type [18].

2.2. Preparation of Clays

Phosphate pre-treatment of the clays was done by mixing the clays (0.5 g for kaolinite and 0.1 g for both montmorillonite and allophane), with 1.0 mM NaH_2PO_4 using 10 mM $NaNO_3$ as a background electrolyte solution and water to reach a final volume of 100 mL. As kaolinite was expected to be less reactive than montmorillonite and allophane, higher solid to solution ratio (0.5 g: 100 mL) was used. Solution pH was maintained at pH 5 by addition of 0.1 M NaOH or 0.1 M HNO_3 during the course of the experiment. The suspensions were shaken on a reciprocal shaker for 24 h followed by centrifuging at 8000 rpm for 25 min. The samples were washed with water to remove excess NaH_2PO_4. The phosphate-clays (P-montmorillonite, P-kaolinite and P-allophane) were immediately used in the form of wet paste in experiments with Pb. Clays pretreated with both P and Pb were prepared by simultaneous addition of P and Pb, by mixing clays (kaolinite (0.5 g) and montmorillonite and allophane (0.1 g), with 1.0 mM NaH_2PO_4 and 1.0 mM $Pb(NO_3)_2$ (equimolar solutions), with 10 mM $NaNO_3$ as the background electrolyte at pH 5. The suspensions were shaken on a reciprocal shaker for 24 h followed by centrifuging at 8000 rpm for 25 min. The samples were then washed with water to remove excess $Pb(NO_3)_2$. The treated clays (P-Pb-montmorillonite, P-Pb-kaolinite and P-Pb-allophane) were immediately used in the form of wet paste in the experiments.

Lead pre-treatment of the clays was done exactly the same as for phosphate pretreated clays, except that 1.0 mM NaH_2PO_4 was replaced with 1.0 mM $Pb(NO_3)_2$. The Pb-clays (Pb-montmorillonite, Pb-kaolinite and Pb-allophane) were immediately used in the form of wet paste in experiments with P. Control clays (montmorillonite, kaolinite and allophane) were prepared in the same way with the background electrolyte and water, but without added P or Pb. The treated and control clays were then used in batch adsorption experiments.

2.3. Lead Adsorption

Adsorption of Pb on treated montmorillonite was achieved by adding a series of initial Pb up to 1 mM to the wet pastes of clay 1) pre-treated with phosphate 2) pretreated with both phosphate and Pb and 3) with no phosphate nor Pb (control clay). The treatments were in duplicate. The suspensions were shaken on a reciprocal shaker for 24 h, at 20°C ± 2°C, before centrifugation at 8000 rpm for 25 min. The supernatant was carefully decanted and analyzed for Pb concentration by atomic absorption spectrophotometer. The amounts of Pb adsorbed were calculated from the difference between initial and final concentrations, and plotted against solution concentration at equilibrium. The same study was repeated with 1) kaolinite and 2) allophane with the same treatments.

2.4. Phosphate Adsorption

Adsorption of phosphate on treated montmorillonite was achieved by adding a series of initial phosphate up to 1 mM to the we pastes of clay 1) pre-treated with Pb 2) pretreated with both phosphate and Pb and 3) with no phosphate nor Pb (control clay). The suspensions were shaken on a reciprocal shaker for 24 h before centrifugation at 8000 rpm for 25 min. Phosphate in the supernatant was analyzed colorimetrically by the ascorbic molybdate method [20]. The amounts of phosphate adsorbed were calculated from the difference between initial and final concentrations, and plotted against solution concentration at equilibrium. The same study was repeated with kaolinite and allophane with the same treatments. The adsorption data were fitted to the Langmuir equation and sorption parameters calculated with the linearized equation (Equation (1)).

$$C/X = 1/X_m K + C/X_m \tag{1}$$

where X = amount of Pb adsorption (μmol·g^{-1}), K = a constant related to binding energy (L·μmol·L^{-1}), X_m = maximum Pb adsorption (μmol·g^{-1}), C = equilibrium Pb concentration (μmol·L^{-1}).

3. Results and Discussion

3.1. Lead Sorption

The adsorption isotherms of Pb on three sorbents (montmorillonite, allophane, and kaolinite) at pH 5 are shown in **Figures 1-3**. The Pb adsorption increased with increasing Pb concentration in all cases. The curves for allophane were obtained with the same solid/solution ratio as that used for montmorillonite (0.1 g: 100 ml). Adsorption isotherms of Pb by three clays mineral demonstrate differences in adsorption capacity (**Figures 1-3**). The component could be classified according to their adsorption capacity: montmorillonite > allophane > kaolinite, as inferred by their CEC values. Similar results were obtained by other authors who study the adsorption of Pb by soil in different cation exchange capacity [21] and in cadmium [22] and nickel [23] and in zinc [24]. The results indicating that the montmorillonite and allophane are important sinks for heavy
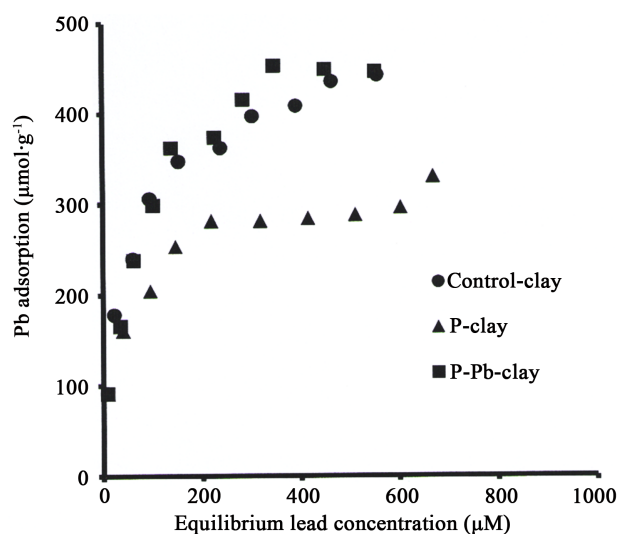
Figure 1. Lead adsorption isotherm on montmorillonite (control), P-montmorillonite and P-Pb-montmorillonite.
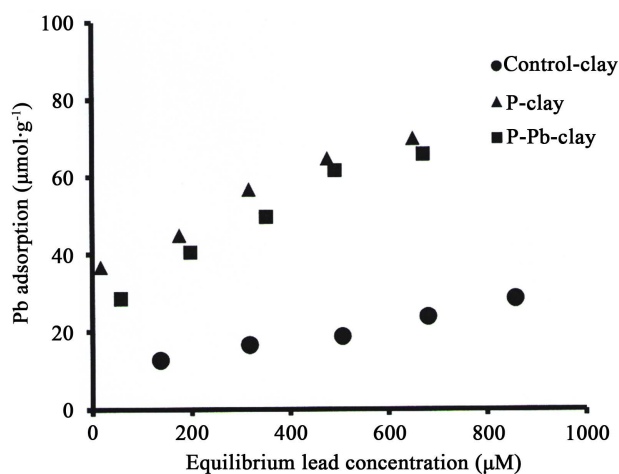

Figure 2. Lead Adsorption isotherm on kaolinite (control), P-kaolinite and P-Pb-kaolinite.
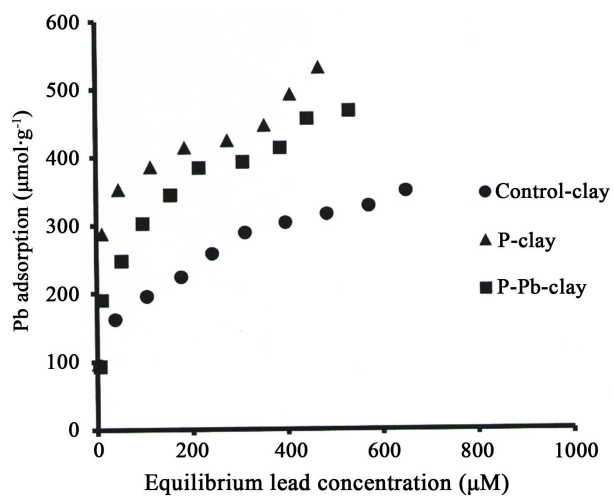

Figure 3. Lead adsorption isotherm on allophane (control), P-allophane and P-Pb-allophane.

metals in soils, due to the fact that they have a large specific surface area. However, kaolinite has a low CEC and, therefore, it is not expected to be an ion-exchanger of high order. The adsorption isotherms of Pb on all three minerals followed Langmuir type. The Langmuir equation parameters are summarized in Table 1. The trends of the Pb sorption isotherms and maximum adsorption on allophane were similar to those of kaolinite. Among all the three minerals, kaolinite had a lower Pb sorption than montmorillonite and allophane which had a similar order of magnitude. The maximum adsorption capacity of Pb in three minerals was in the order: montmorillonite > allophane > kaolinite. Montmorillonite has high Pb adsorption because it has high cation exchange capacity compare with allophane and kaolinite [25] [26]. Adsorption of Pb on kaolinite has been shown to involve both permanent and variable charge sites [27]. [28] and [29] showed significant inner sphere complexation of Pb on kaolinite. Using synchrotron X-ray absorption fine structure spectroscopy study demonstrates the Pb adsorption mostly the inner sphere, probably monodentate Pb complexation at aluminum-oxide surfaces [30]. Figure 3 shows that the Pb strongly adsorbed on nano ball allophane. Allophane was found to adsorb various cations and anions depending upon pH of the soil, cations being adsorbed mostly in high pH silanol groups (negative charges $(Si–O^-)$ at inner surface of the ball). Anions adsorbed at positive charge $\left(Al–OH_2^+\right)$ at low pH at pore sites of the ball of allophane. The allophane strongly adsorbed Pb, this may be Pb ions that were strongly attracted to dissociated silanol group at the inner surface of hallow spherical of nano-ball allophane particle. Molecular orbital calculations with MOPAC AMI basis set indicated that could adsorbed not only on dissociated silanol groups but also with the undissociated silanol groups. The calculations also indicated that when metal ions interacted with undissociated silanol groups, dissociation reaction of the silanol groups accelerated [31].

Table 1. Maximum adsorption (X_m) and binding energy (K) for lead on the three minerals as affected by pre-treatment.

Mineral	Parameter	Control-clay	P-clay	P-Pb-clay
	X_m	500	322.6	500
Montmorillonite	K	0.015	0.023	0.0168
	R^2	0.99	0.99	0.99
	X_m	370.4	500	476.2
Allophane	K	0.014	0.041	0.0225
	R^2	0.98	0.98	0.99
	X_m	37.5	74.1	78.1
Kaolinite	K	0.0027	0.015	0.0674
	R^2	0.89	0.97	0.97

The adsorption isotherm of Pb onto phosphate-pretreated (phosphate adsorbed on clays first then Pb adsorbed to clay surface) by three clays mineral samples as shown in Figures 1-3. These isotherms represent the adsorption behaviorsof Pb on kaolinite and allophane were similar to each other, the amount of Pb was higher as compared with clay free phosphate. Both are different from Pb adsorption amount by montmorillonite. Adsorption of Pb onto clay minerals can occur through two mechanisms: the first, via outer-sphere adsorption, which occurs primarily on basal planes existing in the interlayer of the clay mineral, and the second, via inner-sphere adsorption, which occurs at the amphoteric ligand sites existing on the edges of clay minerals [32] [33] [34] [35]. The adsorption of Pb by montmorillonite at low-ionic-strength occur is consistent with outer-sphere complexation [35]. The phosphate reduced Pb adsorption on montmorillonite, these attributed to the adsorbed phosphate which partially prevented the added Pb penetrating into the interlayer space of montmorillonite, thus, the phosphate can decrease the interlayer of adsorption for Pb [36]. On another hand, phosphate can also lower surface electrostatic potential near the solid surface and therefore, enhance the Pb uptake through outer layer complexes [36]. However, this description does not mean that the adsorption of Pb only occurs as inner-sphere complexes. The adsorption of phosphate causing the increasing in soil negative charge [15] [37] [38]. Kaolinite pretreated with P provides an ideal surface for the metal to specifically react with the P moiety bound to aluminum oxide sorption sites on the surface. Phosphate would increase soil adsorption for heavy metal with positive charges [39]. This was a demonstration for Pb on P-allophane and also for P-kaolinite in this study. Similar results were found on adsorption of Pb on P-kaolinite [15] [16] [17]. The phenomena also supported by many workers in different mineral for example in P-pretreated goethite [11]. It was suggested that enhanced cadmium adsorption was caused by the reduction of the zero point of charge of goethite and surface potential after phosphate adsorption. The study also adopts that the rise in cadmium adsorption on goethite may happen because of a decrease in the electrostatic potential near the solid surface, which arises with the increase in negative charge. Moreover, another possibile explanation was stated by [40] [41] they detected pyromorphite formation, and the pyromorphite was responsible for removal of Pb from solution. The precipitation of pyromorphite in suspension was detected by XRD and identified by both SEM and EBSD.

Furthermore, the simultaneously Pb-P-treated clay was given different amounts of Pb adsorption when compared with the Pb adsorption in P-treatment mineral (Figures 1-3). Phosphorus-pre-treated montmorillonite had a lower Pb sorption than P-free and that simultaneously pre-treated with P and Pb (Figure 1 and Table 1). As shown in these figures, the amount of Pb in the simultaneously Pb-P-treated clay was slightly lower than that P-mineral, in all cases. In the same time, the simultaneously Pb-P-montmorillonite was equal to montmorillonite free-phosphate (Figure 1). The may be attributed to Pb-phosphate in

the simultaneous system forming a different complex solution from the pre-treated system. Therefore, in the simultaneously treated system, these complexes might be adsorbed by some sorption sites that differed from the Pb adsorbing sites. Moreover, as shown in Table 1, the Xm of 500 mmol·kg⁻¹ on montmorillonite free phosphate and 322.2 mmol·kg⁻¹ on P-pretreated clay. The lower Xm value on P-pretreated clay was due to the adsorbed phosphate which partially prevented the added Pb penetrating into the interlayer space of montmorillonite. Nevertheless, in the simultaneous experiments, Xm did not decrease (500 mmol·kg⁻¹), indicating want of kinetic study of the two adsorbates on montmorillonite.

3.2. Adsorption of Phosphate

The adsorption isotherms of P on the three clays mineral samples are shown in Figures 4-6. The P sorption increased with increases of phosphate concentration in all cases. Like for Pb adsorption, phosphate adsorption isotherms on all three minerals followed the Langmuir type. The Langmuir equation parameters are summarized in Table 2. Adsorption isotherms for phosphate onto the three clays mineral samples exhibited differences in adsorption capacity (Figures 4-6). The components could be classified according to their adsorption capacity: allophane > kaolinite > montmorillonite, indicating that allophane is strong adsorbed phosphate. The adsorption of phosphate has been extensively investigated by former workers [37] [42]. The phosphate anion is easily adsorbed on allophonic soils [43] and very strongly adsorbed on the natural nano-ball allophane [44] [45] [46]. The allophane has higher affinity to adsorbed phosphate compare with montmorillonite and kaolinite as of the allophane much of Al-OH and Al–H_2O functional groups on the mineral surface [47]. Aluminol groups, Al-OH or Al-OH_2, are responsible for phosphate and organic anions adsorptions in soils and clay minerals [37]. In the structure of allophane, the aluminol groups are only located at the pores of the wall of the hollow spherules [48].

Table 2. Maximum adsorption (X_m) and binding energy (K) for phosphate on the three minerals as affected by pre-treatment.

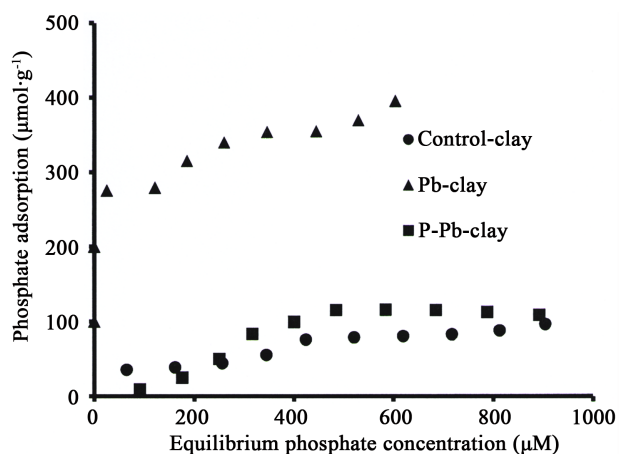| Mineral	Parameter	Control-clay	Pb-clay	P-Pb-clay
Montmorillonite	X_m	144.9	384.6	140.8
	K	0.002	0.0485	0.005
	R^2	0.94	0.99	0.88
Allophane	X_m	322.6	416.7	222.2
	K	0.01	0.0279	0.0032
	R^2	0.98	0.99	0.97
Kaolinite	X_m	106.4	122.0	145
	K	0.009	0.0217	0.014
	R^2	0.97	0.97	0.97

Figure 4. Phosphate adsorption isotherm by montmorillonite (control), Pb-montmorillonite and P-Pb-montmorillonite.
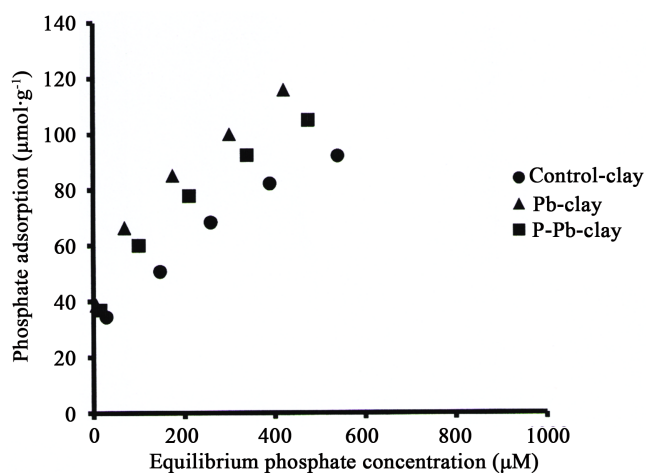

Figure 5. Phosphate adsorption isotherm on kaolinite (control), Pb-kaolinite and P-Pb-kaolinite.
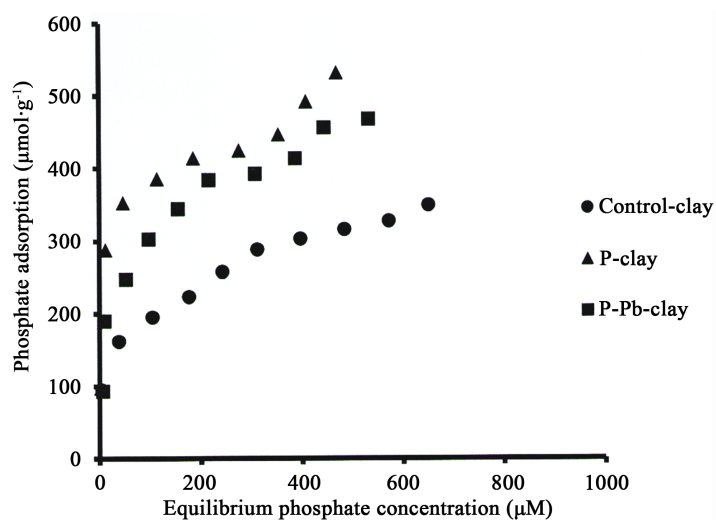

Figure 6. Phosphate adsorption isotherm by allophane (control), Pb-allophane and P-Pb-allophane.

Phosphorus adsorption onto kaolinite may be via an inner-sphere mechanism and also by the formation of Al-P surface precipitates [47]. The reaction of phosphate with permanent charge minerals has received much less attention [49], and generally supposed that it occurs on edge, variable charge regions of the phyllosilicate [37] (Parfitt, 1978). Montmorillonite hardly adsorbs phosphates anions because of it is a lower amount of reactive sites such as Al–OH [50] [51] [52].

The experiments data of adsorption isotherm of phosphate onto Pb-pretreated on three sorbents (montmorillonite, allophane, and kaolinite) are shown in **Figures 4-6**. It is clearly evident that the amount of phosphate adsorption onto the Pb-pretreated clay was higher than the Pb-free clay in all cases. Phosphate minerals play a significant role in regulating the behavior and bioavailability of Pb in soils [53]. The adsorption of Pb first then phosphate may be Pb to a competitive interaction of phosphate with the montmorillonite-Pb complex on montmorillonite surface, which caused breaking of bonds between Pb and the surface and precipitation of pyromorphite. Since the amount of phosphate adsorbed on montmorillonite are usually lower than that found in Pb adsorption, it is expected that the effect of phosphate on Pb adsorption will not be as strong as observed in Pb on phosphate adsorption [49]. The increase of phosphate adsorption in Pb–clay mineral ascribed partly to adsorption of phosphate in mineral and partly to the formation of pyromorphite which is highly stable [14] [54]. The amount of phosphate adsorption for the mixed system was lower than the single system. This indicates competitive adsorption between phosphate and Pb at pore region of allophane where both aluminol and silanol groups exposed.

The amount of phosphate onto simultaneous Pb-phosphate-treated clays onto three mineral (montmorillonite, allophane, and kaolinite) are presented **Figure 4-6**. As shown in these figures, this treatment gave different amounts when they compared with the phosphate adsorption in Pb-pretreated mineral. The simultaneous montmorillonite had a greater P sorption than P-free Pb and pre-treated with Pb (**Figure 4** and **Table 1**). The phosphate adsorption was higher in kaolinite and lower in montmorillonite and allophane. Slightly more phosphate was adsorbed by simultaneously phosphate-Pb-treated kaolinite than Pb pretreated kaolinite. Since Pb and phosphate tend to form Pb-phosphate complexes in co-existing solution, it is likely that more complexes might be formed in the simultaneously treated system than the pretreated system. Therefore, in the simultaneously treated system, these complexes might be adsorbed by some sorption sites that differed from phosphate adsorbing sites in addition to phosphate specific adsorption. Thus, the overall phosphate adsorption was relatively higher in this system. When added simultaneously, the two ions were adsorbed about equally, with the total surface coverage being slightly greater than for either ion alone. Langmuir Xm values of phosphate were 145 mmol·kg^{-1} on montmorillonite, and 385 mmol·kg^{-1} on Pb -pretreated montmorillonite (**Table 2**). The great increase in Xm value in the Pb -pretreated montmorillonite was ascribed to the formation of highly stable Pb-phosphate (pyromorphite) on the surface of

montmorillonite. However, in the simultaneous adsorption experiments, Xm did not increased (141 mmol·kg^{-1}). This also indicates a need for the kinetic study suggested above. Therefore, there are three mechanisms to elucidate the amount of Pb in the simultaneous Pb-phosphate-treated clay was slightly lower than that P-mineral, in all cases, in the same time. The first is adsorption Pb on the clay pretreated surface, the second is partially due to (dissolution-precipitation mechanism) by the formation of Pyromorphite. Similar results were described by [41] [54] [55]. The third is maybe due to the complexes create a new surface and adsorption occur by some sorption sites that differed from phosphate adsorbing sites in addition to phosphate specific adsorption.

4. Conclusion

The adsorption and mutual adsorption isotherms of all three metal ions followed well Langmuir equation. The amount of adsorption of lead on all three minerals has been highest on montmorillonite followed by allophane and then kaolinite, these findings indicating that the clay minerals are important sinks for the lead in soils. The adsorption capacity of lead in clay pretreated phosphate enhance the adsorption, however, the enhancement depends on minerals type. So, clay pretreated phosphate was found to be very good sorbent for the lead for both allophane and kaolinite mineral, whereas adsorption enhancement is not observed onto montmorillonite, the enhancement may be due to increasing negative charge, causing a new surface. Thus, the addition of phosphate is suitable to remediate lead contamination soil, these especially strong in a site of lead contaminated sites especially dominate by both allophane and kaolinite. The order of addition of Pb and phosphate separately in clay pretreated phosphate or clay pretreated Pb or simultaneously addition, gave different amount of adsorption for both phosphate and lead in two systems onto three minerals, thus, extra information on kinetic study for all adsorbate on three minerals are needed. These findings suggesting the actual reactions are more complicated that could be only described by adsorption isotherm and Langmuir equation. Therefore, other techniques such as X-ray diffraction, Scanning Electron Microscopy with energy-dispersive X-ray analyses, and ATR-FTIR and more other highly sophisticated surface analytical performances are essential to find and elucidate the mechanisms of these reactions. Addition to this, more research will be necessary to explore the actual relationships between Pb and Phosphate to another type of clay minerals.

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