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paper text:

1 Studies on the performance of bentonite and its composite as phosphate adsorbent and phosphate supplementation for plant

T Artik Elisa Angkawijayaa, Shella Permatasari Santosob,c,*, Vania Bundjajac, Felycia Edi Soetaredjob,c, Chintya Gunartoc, Aning Ayucitrab, Yi-Hsu Jua,c,d, Alchris Woo Goa, Suryadi Ismadjib,c a Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan b

5 **Department of Chemical Engineering, Widya Mandala Catholic University Surabaya**, Surabaya 60114, **Indonesia** c Chemical Engineering Department, National Taiwan University of Science and Technology, Taipei 10607, Taiwan d **Chemical Engineering Department, National Taiwan University of Science and Technology, Taipei** 10607, **Taiwan**

GRAPHICAL ABSTRACT ARTICLE INFO ABSTRACT Editor: Daniel CW Tsang Organo-bentonite (OrB) was prepared by modifying bentonite with chitosan, and natural surfactant extracted Keywords: from Sapindus rarak fruit. The physical alteration post-modification, performance of phosphates (Pi) adsorption, Organo bentonite and possibility as a Pi-supplementation for plants of OrB were assessed and compared to acid-activated bentonite Phosphate (AAB). The physical alteration due to modification of bentonite was characterized. SEM images were not in- Adsorption dicating significant morphology differences between OrB and AAB. Existence of chitosan layers in OrB causes a Rarasaponin Root elongation decrease in basal spacing as characterized using XRD. The BET surface area of OrB was decreased compared to AAB due to pore coverage by chitosan. Adsorption studies reveal that OrB has a higher adsorption capacity towards Pi

than AAB, which is 97.608 and 131.685 mg/g at 323 K for AAB and OrB, respectively. The H-shape isotherm curve indicates that chemisorption is dominantly controlling the adsorption. The isotherm and kinetics adsorption were well fitted to Langmuir and Pseudo-second order models, respectively. Performance of AAB and OrB as Pi-supplementation was assessed based on growth phenotypes of Arabidopsis thaliana; seedlings show that supplementation of Pi@AAB and Pi@OrB (at half doses) can promote primary root extension. These results also demonstrate the safety of direct disposal of the materials into the soil. *

Corresponding author at: Department of Chemical Engineering, Widya Mandala Catholic University Surabaya, Surabaya 60114, Indonesia. E-mail address: shella_p5@yahoo.com (S.P. Santoso).

. 1. Introduction The importance of phosphorus in biological functions and their es- sential role as a growth-limiting element for plants and animals is un- questionable (Angkawijaya et al., 2017; Gruber et al., 2013; F. Yang et al., 2019; Zhang et al., 2020). In nature, plants are the pivotal source of phosphorus for the animal. Inorganic phosphorus, such as phosphate (Pi), is the most readily available form for plant uptake (Młodzińska and Zboińska, 2016; Raghothama, 1999; Yao et al., 2013). While at a certain level, the presence of Pi is crucial, contamination of extremely high levels in the aquatic environment can be very deteriorating. At a Pi level of 0.02 mg/L, it triggers a boom-growth of algae that leads to eutrophication and caused oxygen depletion (P. S. Kumar et al., 2019; R. Li et al., 2016). While under normal circumstances, Pi is very im- mobile in the soil, eutrophication is still considered as a persistent threat due to the disposal of Pi-containing wastewater. Reportedly, industrial wastewater from the H3PO4 wet process, canned fish, dairy product, and anodized industry contain up to 5069 mg of Pi per liter of wastewater (Bacelo et al., 2019). Not limited to industrial waste, an- thropogenic activities also contribute to increasing Pi levels in water bodies, i.e., domestic wastewater (5−20 mg/L), swine farm (100−987 mg/L), and urine (470−1070 mg/L) (Bacelo et al., 2019). Thus, a treatment process is needed to control the Pi level in the water body to avoid eutrophication. Several methods have been developed to treat wastewater con- taining Pi, namely physical, chemical and biological treatment; but they might also be hybridized (G. Li et al., 2018; F. Xie et al., 2016; Q. Xie et al., 2017). In physical treatment (i.e., sorption), removal of Pi in- volves the use of adsorbent and adsorptive media with potential sorp- tion capacity; adsorbent prepared from biochar, biomass, and clay minerals are widely used (Mdlalose

19**et al., 2018**; Peng **et al., 2019**; Robalds **et al**., 2016; F. Xie **et al**., 2016; Q. Xie **et al**., 2017; F. Yang **et al**., 2019; Q. **Yang et al**., 2018; Zhang **et al**

., 2020).

1**On the other hand, the Pi removal by**

chemical treatments usually involves pre- cipitation and coagulation, which are carried out by the addition of chemicals such as aluminum sulfate, iron sulfate, and sodium aluminate (Mollah et al., 2004). Biological treatment involves the use of biofilm- forming organisms (i.e., algal-bacteria hybrid) to trap Pi and then precipitate it (Bunce et al., 2018). Various issues may arise from these treatments. Not only the added-chemical might be harmful to the en- vironment, the efficiency of the treatment only served at high Pi con- centration, and the recovery of Pi can be challenging. In biological treatment, time and the requirement for large processing area are the limiting factors. Meanwhile, the limitations of physical methods (par- ticularly adsorption) revolve around the availability of suitable sorption matrix with high adsorption capacity. This

limitation is relatively easier to address given the massive option of modifiable-material for ad- sorption matrix. Furthermore, the recoverability of Pi is one of the crucial points in its treatment method; this is since the natural pro- duction of Pi from phosphorous is a slow process. Therefore, exaggerate treatment (or removal) of Pi can lead to its scarcity. The advantage of adsorption is that the adsorbed substances can be easily recovered. This study aims to develop an economical dual-purpose bentonite composite composed of natural materials that may act as a Pi-adsorbent and Pi-supplementation for plant nutrients. The natural materials such as bentonite, rarasaponin, and chitosan were used. The adsorptive ability of the synthesized composites against aqueous reactive Pi spe- cies was investigated. The novelty in this study derived from the utili- zation of environmentally friendly materials, thus facilitate direct dis- posal of post-adsorption bentonite to the soil without damaging effect on the environment. These findings will solve the drawback raised from the utilization of synthetic polymer-based adsorbents (e.g., PVC and resin) that are not readily degraded. Moreover, the potential of the Pi- loaded composites as a Pi-supplementation for plant growth was proven in this study.

2. Materials and methods 2.1. Materials Bentonite used in this study was obtained from a mining site in Pacitan, East Java, Indonesia. Bentonite

is chosen over other types of clay (such as struvite, ferrihydrite, and goethite) due to its abundance in many mining sites, especially in Indonesia. The bentonite was ob- tained in big chunks, which then crushed into a fine powder (+180/- 200 mesh). The bentonite has cation exchange capacity of 45 meq/100 g; and dominantly composed of SiO_2 (62.0 %) followed by Al_2O_3 (19.2 %), CaO (3.6 %), Fe_2O_3 (3.0 %), Na_2O (2.2 %), MgO (2.0 %), K_2O (1.8 %), MnO (0.2 %), and TiO_2 (0.1 %). Rarasaponin was extracted from Sapindus rarak using methanol as a solvent (Putro et al., 2019). Other chemicals used in this study are chitosan (85 % deacylated) purchased from C.V. Nura Jaya, East Java, Indonesia; H_2SO_4 (98 % purity), K_2HPO_4 (99 % purity), and acetic acid glacial (CH_3COOH, 99.85 % purity) purchased from Sigma Aldrich (St. Louis, USA) through a chemical distributor in East Java, Indonesia. Deionized water with 18.3 MΩ cm obtained from RDI Reverse Osmosis Deionizer System equipped with 50GPD UV ultrapure water maker and conductivity- meter (purity EC-410) were used throughout the experiment. 2.2. Preparation of adsorbents

Acid-activated bentonite (AAB) and organo-bentonite

(OrB) were used as adsorbents. AAB was prepared by immersing bentonite into 1.5 M H_2SO_4 solution for 2 h at 90 °C, as reported by Laysandra et al. (Laysandra et al., 2019). The AAB was pulverized to a fine powder (+80/-100 mesh) and

kept in an airtight container. The OrB was

pre- pared as follows: bentonite and rarasaponin (1:10 w/w) were mixed in 50 mL deionized water. The mixture was heated at 80 °C for 60 min under stirring 300 rpm, followed by irradiation using the

microwave at a heating power of 700 W for

180 s (Santoso et al., 2017). Prior to the addition of chitosan solution to the rarasaponin-bentonite mixture, 1 wt % of chitosan powder was dissolved into 2.5 % (v/v) acetic acid solu- tion and was stirred continuously at 80 °C for 60 min. The rarasaponin- chitosan-bentonite (OrB) mixture was then stirred for another 3 h, at 80

°C then dried in a 100 °C oven for 2 d. The obtained solid OrB was pulverized to a fine powder (+80/-100 mesh) and kept in an airtight container. 2.3. Adsorbent characterization SEM analysis was conducted to collect the surface topography images. A JEOL JSM-6500 F (Japan) SEM

3**at an accelerating voltage of 15.0 kV** was used for **the**

analysis.

23**Prior to the** analysis, **the samples were coated with**

Pd/Pt coating using an auto fine coater JEOL JEC- 3000FC (Japan). XRD analysis was performed to record the crystallinity pattern of the samples. The XRD measurements were conducted on

1**a Bruker D2 Phaser diffractometer using Cu Kα radiation**

(λ =1.5418 Å). The surface functional group in adsorbent before and after adsorptions were investigated based on its Fourier Transform Infrared (FTIR) ob- tained from Shimadzu IRTracer-100, with

5**KBr pellet was used as the background**. Nitrogen (N2) adsorption **and** desorption analysis **were**

carried out using Brunauer-Emmett-Teller (BET) BelsorpMax analyzer (Japan).

17**The samples were degassed using Belprep-vacII** at 150 °C **for** 4 **h before the analysis**

to ensure total removal of all pre-occurring ad- sorbed species on the material surface. 2.4. Phosphate sorption 2.4.1. Effect of pH Pi solutions were prepared by dissolving K2HPO4 in DI water at a concentration of 200 mg/L. The prepared Pi

10**solution was distributed** into **a series of Erlenmeyer** flask, each containing **50 mL solution**

. The pH of each flask was adjusted to a certain pH using 0.1 M HCl or NaOH solution, between pH 3–12. 20 mg of adsorbent sample was introduced into a pH-adjusted solution. This test was done to assess the adsorption ability of the synthesized composite at different pH. The flasks were then put into

20**a shaking water bath for 24 h. The**

data obtained from this analysis were used to determine the optimum pH for Pi adsorption using AAB and OrB. 2.4.2. Adsorption isotherm

10A series of capped **Erlenmeyer** flask containing **50 mL of** Pi **solution** (200 mg K2HPO4 **in**

1 L DI water) were prepared. The

3**pH of the solution was adjusted to 6**

and 8 before adsorption using AAB and OrB, re- spectively. A different mass of adsorbent samples (1, 5, 10, 20, 30, 40, 45, and 50 mg) was then introduced into each flask.

9**The flasks were placed** on **a shaking water bath at a** maintained **temperature**

of 30, 40, or 50 °C. The adsorption was done for 24 h, then an aliquot of the solution was taken to determine the residual amount of Pi. 2.4.3. Adsorption kinetics 20

1**mg of adsorbent** sample **was** introduced **into a series of**

capped Erlenmeyer flask containing Pi solution (200 mg K2HPO4 in 1 L

3**DI water). The pH of the solution was adjusted to 6**

and 8 before adsorp- tion using AAB and OrB, respectively. The adsorption kinetics of Pi onto the adsorbent sample was examined

20**at three different temperatures of 30**, 40, **and** 50 °**C**. An aliquot of **the** solution **was**

taken from a flask at a different time interval (multiple of 15 min for the first 1 h, multiple of 30 min for the next 2 h, and 60 min) to determine the amount of Pi adsorbed. 2.4.4. Residual Pi concentration measurement The Pi-adsorbed composite was separated from the residual Pi so- lution

7**by centrifugation at 3000 rpm for** 3 **min**. Subsequently, **the**

1**Pi solution was filtered using a 0**.45 **μm** pore size membrane **syringe filter to** remove **the**

small adsorbent fragments or other small particles. The residual Pi concentration was then measured using the spectro- photometric method using ammonium molybdate-based reagent. The Pi containing solution will produce a colored solution with maximum absorbance at 880 nm. Details of the measurement procedure can be found elsewhere (Lowry and Lopez, 1946). 2.5. Adsorption data fitting A graphing and fitting software, SigmaPlot version 12.5 build 12.5.0.38 (Systat Software, Inc.), was used to analyze the adsorption

data. A data fitting based on adsorption mathematical models was performed using the dynamic curve fitting function; this is to examine the adsorption mechanism and behavior of Pi onto the adsorbent sample. The sum squared error (R2) calculated from the data fitting was evaluated to determine the best adsorption model that can well-corre- late the data. Analysis of the statistical significance was determined using one-way ANOVA and Student's t-test by the GraphPad Prism program. 2.5.1. Adsorption isotherm

> 17**The adsorption isotherm plots were constructed from the**

qe versus Ce data points. The parameter

> 22**qe (mg/g) is the equilibrium amount of adsorbate adsorbed**, and **Ce** (mg/**L**) **is the** residual amount **of adsorbate**

at equilibrium. The value of qe is calculated based on Eq. (1) as follow: qe = C0 − Ce m ×V (1) where C0 (mg/L) is the initial concentration of adsorbate, m (g) is the mass of adsorbent, and V (L) is the total volume of adsorption system. The following multiple-parameters models (Table 1) were used to correlate the isotherm adsorption of Pi onto the adsorbents. As shown in many studies, Langmuir and Freundlich are the classic isotherm models Table 1 The fitting models used for adsorption isotherm or kinetics, and the corre-sponding mathematical expression. Fitting model Equation Fitting parameter (unit) #Eq. Isotherm models Langmuira Freundlichb Redlich-Petersonc Sipsd Kinetics models Pseudo-first ordere Pseudo-second orderf qe = 1qL+KKLLCCee RL = 1+KLC0 1 qe = KFCe1\nF qe = 1+KRaPRCPeCeβ qe = 1q+SKKSSCCenenSS qt = qe1(1 − e−k1t) qt = qe2 √ 1+qeq2ek22kt2t⁄ ⌡ qL (mg/g) KL (mg/L) RL KF (mg/g)(L/mg)−n n F KRP (L/g) aRP (L/mg) β qS (mg/g) KS (L/g) nS

> 8**qe1 (mg/g) k1 (1/min) qe2 (mg/g) k2 (g/mg min**

(2) (3) (4) (5) (7) (8) a (Langmuir, 1916). b (Freundlich, 1932). c (Hamdaoui and Naffrechoux, 2007). d (Belhachemi and Addoun, 2011; Hamdaoui and Naffrechoux, 2007). e (Azizian, 2004; Lagergren, 1898). f (Azizian, 2004; Ho and McKay, 1999). which found to satisfy almost all adsorption systems (Belhachemi and Addoun, 2011; Hamdaoui and Naffrechoux, 2007). Langmuir model calculation assumes that the adsorbent surface is homogeneous. The constant qL and KL represent the maximum adsorption capacity and adsorption affinity constant, respectively. The dimensionless parameter RL expresses the favorability of the adsorption. On the other hand, the

> 13**Freundlich model is based on the assumption that the** adsorbent **surface is heterogeneous. The**

parameter KF is a Freundlich parameter, which accounts for the

> 1**adsorption capacity**, while **nF is a dimensionless** con- stant indicated **the favorability of adsorption**

. Redlich-Peterson and Sips model is the hybrid of Langmuir and Freundlich model. The hybrid models are applicable for both homogeneous and heterogeneous sys- tems; they

1**also can be used to confirm the Langmuir** and **Freundlich** model approaches. In **the**

Redlich-Peterson model, the adsorption ca- pacity is shown from the ratio of KRP to aRP (qRP = KRP/aRP). The value of parameter β can be used to determine the adsorption behavior. The adsorption obeys Langmuir

14**as β = 1, and Freundlich as aRP**

Ceβ > 1. In

14**Sips model, qS** shows **the adsorption capacity**

. The parameter KS is a constant of equilibrium. Parameter nS has a similar property with parameter β form Redlich-Peterson. The Sips model approaches Lang- muir as nS = 1, and Freundlich as Ce or KS 0. → 2.5.2. Adsorption kinetics The adsorption kinetics plots were constructed from the qt versus t data points. The parameter

8**qt (mg/g) is the amount of** adsorbate ad- **sorbed at** a certain **time**, and **t (min) is the** interval time **of**

adsorption. The value of qt is calculated based on Eq. (6) as follow: qt = C0 − Ct m ×V (6) where Ct (mg/L) is the residual concentration of adsorbate at time t. In many kinetic adsorption studies, the

5**Pseudo-first order and Pseudo-second order** (Table 1) **models are** sufficiently satisfied with **the**

adsorption data points. Both models can suggest solute adsorption rates in solutions (Ho and McKay, 1999; Lagergren, 1898). Both models provide an estimation of the equilibrium amount of adsorbate (solute) absorbed in the system under study, which is expressed in the para- meters qe1 and qe2 for Pseudo-first order and Pseudo-second order, re- spectively. Furthermore, both models also provide the rate coefficient values k1 (

18**Pseudo-first order) and** k2 (**Pseudo-second order). The** con- stant k1 **is** a combination **of**

adsorption (kads) and desorption (kdes) rate constants, which linearly depend on the initial concentration of ad- sorbate. Differently, the constant k2 is a complex function of the initial concentration of adsorbate (Azizian, 2004). The goodness of fit was analyzed using the adjusted determination coefficient (Radj2) instead of the coefficient of determination (R2). Radj2 can depict the goodness of fitting better than R2 since its calculation takes into account the degree of freedom from experimental data and also from the model. 2.6. Arabidopsis thaliana growth media supplementation

1A. thaliana Columbia-0 ecotype was used as the model plant for the

applicational study of Pi-adsorbed-OrB and AAB as a soil supplement. For this purpose, we prepare 4 different media: Pi containing media (P +), Pi starved media (P-), P- media supplemented by Pi-adsorbed-AAB (Pi@AAB), and P- media supplemented by Pi-adsorbed-OrB (Pi@OrB). The media were prepared according to previous publications (Angkawijaya et al., 2017; Estelle and

4Somerville, 1987; Nakamura et al., 2005

) where its

4containing 0.8 % phosphate-free agar (Gelrite Pure, Kelco), 1% sucrose, and 20 mM MES buffer (pH 6.0), with 1 mM

KH2PO4 for P + or without KH2PO4 for P-

1media. The A. thaliana seeds were germinated and grown

on these 4 media under the

23continuous light condition at 22 °C. After 10 days, the

seedlings grown on Pi@AAB and Pi@OrB were observed and compared to the one grown on P + or P- media. For this observation, 2 plates were prepared for each condi- tion of the media, with 8 seeds were planted on each plate.

113. Results and discussion 3.1. Adsorbent characterizations The obtained SEM images of

AAB and OrB were depicted in Fig. 1. No significant surface morphology difference can be observed from both images. Briefly, both AAB and OrB seem to have foliated structures in several areas and similarly rough-surface. However, in closer ob- servation, the OrB (Fig. 1d) showed a slightly less-rough surface com- pared to AAB (Fig. 1b). This is caused by the presence of a thin layer of chitosan that envelops the clay particles. The N_2 adsorption-desorption curves of AAB and OrB are given in Fig. 2a, includes some features associated with mesoporous materials. It is observed that AAB has smaller pores than OrB; this is evident from continuous (and more extended) pore filling at lower relative pressures (at $p/p° \rightarrow 0$). The adsorption branch shows a low slope region, which suggests multilayer adsorption on the pores, this region is observed at $p/p° = 0.06 – 0.43$ for AAB and $p/p° = 0.03 – 0.44$ for OrB. The OrB appears to have a more extended low slope region, which implies that a more layered region formed by chitosan. The pore condensation region that forms a hysteresis is then observed. According to all observed features, the AAB and OrB have a Type IV isotherm with hysteresis loop type H4. The hysteresis loop type H4 indicates that the adsorbents contain complex pores, which causes the desorption process to be de- layed (Sotomayor et al., 2018). The calculated BET parameters, according to the N_2 adsorption- desorption plot, are given in Table 2. The mean

pore diameter of AAB is 6.392 nm, and OrB is 12.664 nm, which confirms the mesoporous pore size of the materials. AAB showed higher surface area (aa = 162.350 m2/g) than OrB (as = 32.029 m2/g), indicates that the addition of chitosan might block the pores, thereby reducing the surface area. Despite the reduction of surface area, OrB provides additional func- tional group which promotes the adsorption capacity; this is shown in the functional groups characterization and adsorption experiments later. The XRD crystallinity patterns of AAB and OrB are depicted in Fig. 2b. The XRD peaks of OrB emerge dominantly from the contribu- tion of the bentonite. Peaks those correspond to montmorillonite, quartz, magnesite, and calcite were observed in both AAB and OrB sample. A single characteristic diffraction peak at 2 θ = 2–10° was observed for AAB and OrB, where this peak indicates the basal spacing Fig. 1. SEM images of (a, b) acid-activated bentonite (AAB) and (c, d) chitosan-rarasaponin-bentonite (organo-bentonite, OrB) at different spots. Fig. 2. (a) N2 sorption plot, (b) XRD pattern, and (c) TG/DTG curve of

16**acid-activated bentonite (AAB) and** chitosan-**rarasaponin-bentonite**

(organo-bentonite, OrB). Table 2 BET parameters for

16**acid-activated bentonite (AAB) and** chitosan-**rarasaponin- bentonite**

(organo-bentonite, OrB). BET Parameter Adsorbent AAB OrB Vm (cm3 (STP)/g) as,BET Mean pore diameter (nm) 37.300 162.350 6.392 7.359 32.029 12.664 (d-spacing) of the silicate layers. The d-spacing for AAB was measured at 2 θ = 5.91°, with a value of 7.49 Å. The d-spacing for OrB was slightly shifted to the higher angle 2 θ = 6.21° with the value of 7.12 Å. While the presence of surfactant postulated to provide an intercalation effect that may improve the d-spacing of bentonite (Kurniawan et al., 2011), rarasaponin-containing OrB has smaller d-spacing than AAB. This indicates that the incorporation of chitosan constricted the inter- layer galleries of AAB. The thermal gravimetric analysis curves of AAB and OrB are illu- strated in Fig. 2c, includes TG and DTG curves. The curves related to AAB show mass losses of 4.23 % and 2.21 %

14**in the temperature range of 30**−140 °**C and**

320−500 °C, respectively. The endothermic peak in the range of 30−140 °C refers to the removal of water molecules that originated from surface humidity and water molecules coordinated to the interlayer of AAB. Meanwhile, the endothermic peak in the range of 320−500 °C occurs due to the de-hydroxylation of the silicate layer and removal of hydroxyl groups. Curves related to OrB show more stages of thermal degradation, specifically at the temperature of 30−100 °C (2.30 %), 110−160 °C (1.11 %), 170−360 °C (8.47 %), and 370−500 °C (4.23 %). The stages

12**in the range of** 30−100 °**C and** 110−160 °**C** correspond to **the** removal **of**

humidity and coordinated water, re- spectively. The loss of water molecules occurs gradually due to the presence of chitosan, which forms more complex layers. The thermal degradation of chitosan signifies by the endothermic peak in the range of 170−360 °C (S. Kumar and Koh, 2012). The final stage of thermal degradation in the range of 370−500 °C occurs due to the same phe- nomenon in AAB, and also the degradation of the remaining chitosan residue (S. Kumar and Koh, 2012). Fig. 3. Effect of pH on the adsorption (uptake) of phosphate using the investigated adsorbent, AAB, and OrB. Different letters indicate a sig- nificant difference with p < 0.05. The black letters indicate the significance of OrB uptake at various pH, while the gray capitalized letters represent the significance of pH in the adsorp- tion capacity of AAB. The red asterisks indicate a significant comparison of OrB to AAB at the same pH

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103.2. Effect of pH on the adsorption

process In this work, adsorption also refers to adsorbate uptake, since as the adsorbate molecules are being attached on adsorbent as they are ad- sorbed. pH value is an essential factor influencing many adsorption processes, adsorption, which takes place at an unsuitable pH will result in low adsorption efficiency. pH is closely related to the degree of io- nization of the adsorbate and surface charge of adsorbent; the adsorp- tion efficiency will be better if both have different charges.

11The surface charge of adsorbent can be determined from the

pH-PZC value; where, positive surface charge occurs when pH solution < pH-PZC and vice versa (Milonjić et al., 1983). As determined using the pH-drift method, the pH-PZC of AAB is 5.16, and OrB is 7.23. Meanwhile, Pi is known as an anion, which has a negative charge at all pH range. The negative charge of Pi becomes higher as the pH solution increases. Theoretically (judging from the pH-PZC adsorbent and anionic properties of the adsorbate), the optimal adsorption should fall within the acidic pH range (i.e., less than 5). However, the investigation result (Fig. 3) shows that the removal of Pi was optimized at pH of 5–6 for AAB and pH of 7–8 for OrB; that is close to the pH-PZC of each ad- sorbent. This is because, at pH > 5, Pi as adsorbate is in the form of more negative species, that is, HPO_4^{2-}; meanwhile at pH < 5, the less negative $H_2PO_4^-$ species were more dominant (Bacelo et al., 2019). The presence of more negative adsorbate species provides better electro- static interaction with the adsorbent. Obviously, at more alkaline pH, both adsorbate and adsorbent possess negative charge; and thus, re- pulsive behavior is more dominant. 3.3. Adsorption mechanism of Pi onto adsorbents FTIR analysis was carried out to get an idea of the mechanism of adsorption through the functional groups shifting before and after Pi adsorption, as shown in Fig. 4. For all samples, characteristic peaks of bentonite can be observed at 470, 524, 918, 1042, and 3618 cm−1 which respectively refer to Si-O-Si bend, Al–O–Si bend, Al–Al−OH bend, Si-O-Si stretch, and Al(Mg)–O–H stretching. The incorporation of chitosan was displayed by the occurrence of CeN stretch and NH2 of amino group at 1096 and 1553 cm−1 in OrB spectra. Additional peaks at 1382 cm−1, which refer to the P]O stretch of organic phosphates, can be observed in Pi@AAB and Pi@OrB; this confirmed the adsorption of Pi on AAB and OrB. Besides the peak of P]O stretch, Pi adsorption to OrB caused a shift of CeN stretch and NH2 of the amino group to 1088 and 1529 cm−1, respectively. After Pi adsorption, the peak of OeH stretch was intensified and shifted from 3432 cm−1 for AAB and 3442 for OrB to 3409 cm−1 (Pi@AAB) and 3417 cm−1 (Pi@OrB). These peaks shift confirmed the involvement of the OeH group in the adsorption of Pi onto AAB and OrB. According to the analysis of pH-PZC and the shifting of functional groups (before and after Pi adsorption), the possible adsorption me- chanism of Pi is illustrated in Fig. 5(a) for the AAB system and Fig. 5(b) for OrB system. In the AAB system, the excessive H+ ion due to acid activation of bentonite caused further protonation of the silanol groups of bentonites; thus, positive-charged groups occurred. The protonated groups then helped the adsorption of Pi through electrostatic interac- tion. Similar to AAB, the silanol group of bentonites in OrB also pro- tonated in the solution. However, only minor protonation of the silanol group is occurring in OrB due to the absence of excessive H+ ions. While the addition of rarasaponin in OrB triggered intercalation of bentonite, their availability might not be the contributor to the en- hanced Pi adsorption. Instead, the presence of chitosan molecules on OrB, which provides amine functional groups on the material surface. These amine groups can be protonated to –NH3+ form, which later promotes the Pi binding through electrostatic interaction. The physical adsorption of Pi further supports this interaction onto

the surface of OrB. 3.4. Adsorption isotherm The effect of adsorption isotherm of Pi on AAB and OrB was investigated at three different temperatures, that is 303, 313, and 323 K. An endothermic adsorption behavior was observed from the adsorption using both tested adsorbents. Thus, the higher temperature was more favorable for the adsorption to proceed. Isotherm data fitting using several models was run prior to know the adsorption behavior and to quantify the isotherm parameters. A nonlinear fitting was conducted on the isotherm data; this is since a linear fitting may create data distor- tions during the transformation of data sets (Motulsky and Ransnas, 1987). The plots of isotherm data fitting into various models were presented in Fig. 6 for the AAB and OrB system. The adsorption plots of Pi onto AAB and OrB show a one-step H- pattern curve, where high-affinity isotherm (qe > > 0) was observed at the beginning of the equilibrium curve. The H-pattern curve indicates that the adsorption system is dominated by chemisorption behavior and that electrostatic forces drive it. The occurrence of the (not strict) plateau at high adsorbate concentration indicates that the adsorbent saturation has occurred; and, it can be expected that the Langmuir and Langmuir-combination models (i.e.,

3**Redlich-Peterson and Sips**) could satisfy **the adsorption**

system. A good correlation of the isotherm data to the Langmuir and Langmuir-combination models also can be noted from the higher value of the adjusted determination coefficient (Radj2) compared to Freundlich fitting (Table 3). The highest adsorption capacity achieved from the batch adsorption Fig. 4. FTIR spectra of acid-activated bentonite (AAB) and chitosan-rarasaponin-bentonite (organo-bentonite, OrB) before and after Pi adsorption (Pi@AAB and Pi@ OrB). Fig. 5. Illustration of the

1**possible mechanism of Pi adsorption** onto (**a**) AAB **and (b**

) OrB at pH close to pH-PZC (i.e., pH > 5). experiment was recorded as qe (exp) value in Table 3. The qe (exp) showed that OrB could adsorb a higher amount of Pi compared to AAB at all investigated temperatures. The highest qe (exp) for AAB and OrB is achieved at the adsorption system at 323 K; that is 97.608

18**mg/g and** 131.685 **mg/g for** AAB **and** OrB, **respectively**. Also, note that **the**

value between qe (exp) and adsorption capacity calculated using the Langmuir model (qmax) and the Sips model (qS) has a difference of less than 10 %. This can be pointed out as a sign that the data points in the batch ad- sorption experiment have almost reached the plateau condition. Meanwhile, the Redlich-Peterson model is failed to describe the max- imum adsorption capacity of the system under investigation. This can be seen from the difference in the value of qRP which is very far Fig. 6. Phosphate (Pi) adsorption isotherm data (C0 = 200 mg/L, T = 303, 313, 323 K) and fitting of: (a-d) acid-activated bentonite (AAB) at pH of 6, and (e-f) organo-bentonite (OrB) at pH of 8. different from qe(exp). It has been evaluated that Pi adsorption onto AAB and OrB obeys Langmuir and Sips model. The Sips model is a three-parameters model that does not provide a direct insight to justify the experimental data. The models

1**can be used to confirm the satisfactory of the Langmuir or Freundlich fitting. Based on the fitting results, the nS value** (Sips model) **of all the adsorption systems is close to 1**, indicates **their better** ap- proach **to the Langmuir model. Furthermore, the KS of the Sips model does not show zero value, which confirms the Langmuir approach**

(Belhachemi and Addoun, 2011; Hamdaoui and Naffrechoux, 2007). Although it has been evaluated that Pi adsorption on AAB and OrB obeys the Langmuir model, it is still interesting to evaluate each para- meter of the other models to reveal the suitability of the adsorption system with Langmuir. The nF parameter of the Freundlich model shows a value

11**in the range of** 2–**10**, which **indicates** favorable **adsorption**. The adsorption system **is** not **favorable**

when the nF value is less than 2 (Hamdaoui and Naffrechoux, 2007).

3**The favorability** of **the adsorption also can be** assessed **from the** RL **value of the** Langmuir **model**. The RL **values**

of all systems lie between 0 < RL < 1, indicating that the ad- sorption is favorable (Hamdaoui and Naffrechoux, 2007). Redlich- Table 3 The calculated parameter values of the isotherm fitting models. Peterson is a three-parameter model; similar to the Sips model, and it does not provide a direct insight to justify the experimental data. The exponent β values of the Redlich-Peterson model are close to 1, in- dicates a better approach to the Langmuir model (Belhachemi and Addoun, 2011; Hamdaoui and Naffrechoux, 2007). The utilization of bentonite-based materials to adsorb Pi has been reported in several studies (Table 4). The most recent studies proposed modification of bentonite using metal ions to increase the adsorption capacity of Pi. For instance, some transition metal ions were used to modify bentonite, including Co, Ni, and Fe. The Co-, Ni-, and Fe-mod- ified bentonite can adsorb Pi up to 46.95, 29.07, and 20.88 mg/g, while unmodified bentonite is only able to adsorb 6.57 mg/g (Mdlalose et al., 2018). Modification of bentonite using Zr metal ion was reported to have an adsorption capacity of 13.40 mg Pi/g (Lin et al., 2018). Further modification of Zr- bentonite using Mg metal ion succeeded in in- creasing the adsorption capacity of Pi to 16.00 mg/g (Lin et al., 2020). Modification of bentonite using metal ions is

12**proven to be** able **to** in- crease **the adsorption capacity of**

Pi. Still, the buildup (and disposal) of materials containing metal ions may have the potential to damage the environment and can cause metal poisoning. The use of natural Model Parameter AAB OrB

1**303 K** 313 **K** 323 **K 303 K** 313 **K** 323 **K**

– Langmuir qE (exp) qmax KL RL Radj 2 SSE 76.502 83.816 0.024 0.172 0.998 12.978 88.121 115.387 0.030 0.143 0.994 34.654 97.608 119.255 0.038 0.116 0.996 28.203 114.212 135.425 0.042 0.106 0.997 30.469 117.633 140.238 0.048 0.094 0.997 34.714 131.685 149.399 0.055 0.083 0.998 31.583 Freundlich KF nF Radj 2 SSE 7.851 2.049 0.979 112.869 14.041 2.525 0.975 153.682 18.006 2.762 0.976 179.247 23.156 2.958 0.975 240.573 23.357 2.817 0.969 347.317 32.363 3.367 0.987 166.119 Redlich-Peterson qRP β Radj 2 SSE 136.588 1.059 0.997 12.299 188.667 1.087 0.996 23.671 377.714 1.244 0.996 18.694 139.389 0.956 0.997 28.176 199.600 1.071 0.997 27.652 219.455 1.093 0.997 22.455 Sips qS KS nS Radj 2 SSE 99.221 0.021 1.060 0.997 12.082 99.562 0.012 1.355 0.997 16.320 110.262 0.025 1.182 0.997 20.595 124.726 0.025 1.219 0.998 16.907 130.496 0.034 1.171 0.998 22.188 156.920 0.069 0.892 0.998 21.111 Table 4 Pi adsorption performance on modified bentonite (Bent) adsorbents. Adsorbent Adsorption experiment Ref Condition Qmax (mg/g) Best fitted model Fe-Bent Ni-Bent Co-Bent Zr-Bent ZrMg-Bent Fe-

Al-Bent Acid and heat-treated Bent AAB OrB pH = 3 20.88 (at 298 K) C0 = 1000 mg/L KH2PO4 29.07 (at 298 K) 46.95 (at 298 K) pH = 7 13.40 (at 298 K) 16.00 (at 298 K) pH = 6.5 8.33 (at 298 K) C0 = 250 mg/L KH2PO4 pH = 3 20.37 (at 318 K) C0 = 150 mg/L KH2PO4 pH = 6 76.502 (at 303 K) C0 = 200 mg/L KH2PO4 88.121 (at 313 K) 97.608 (at 323 K) pH = 8 114.212 (at 303 K) C0 = 200 mg/L KH2PO4 117.633 (at 313 K) 131.685 (at 323 K) Langmuir (Mdlalose et al., 2018) Langmuir (Lin et al., 2020) Langmuir-Freundlich (Yaghoobi-Rahni et al., 2017) Langmuir (Tanyol et al., 2015) Langmuir This study Langmuir This study components as adsorbents for Pi (i.e., OrB) is still rare or has not been reported, which is highlighted in this study. OrB can be more en- vironmentally friendly than metal-modified bentonite adsorbents, the natural component used to prepare OrB allows direct disposal to the ground without damage potential. In addition, the adsorption capacity of Pi provided by OrB (i.e., 131.685

12**mg/g) is** much **higher than that of** metal-modified and **unmodified**

bentonite; this show the superiority of OrB in Pi adsorption from aqueous solution.

21**3.5. Adsorption kinetics Pseudo-first order and Pseudo-second order** fitting **were** used **to** quantify **the** rate **of adsorption**

(Ikhtiyarova et al., 2012). The adsorp- tion kinetics plot (Fig. 7) indicates rapid adsorption in the first 30 min. This phenomenon is very common for adsorption systems that begin with high adsorbate concentrations. Rapid adsorption at the beginning of adsorption also shows that the electrostatic force drives the inter- action between the adsorbent and adsorbate. Adsorption occurs in- stantly because the active sites of the ligand are still empty and have a high affinity for the opposite-charged adsorbate molecule (Q. Yang et al., 2018). Then, the adsorption rate starts to slow down, and a plateau is reached along with the reduction of the active sites of the adsorbent. Based on the kinetics models fitting results (Table 5), it is indicated that the adsorption system of Pi onto AAB and OrB obey

13**the Pseudo- second order** instead of **the Pseudo**-first **order**. This **is** shown from **the**

Table 5 The calculated parameter values of the isotherm fitting models. Model Parameter AAB 303 K 313 K 323 K OrB 303 K 313 K 323 K – Pseudo-first order Pseudo- second order qe (exp) 45.123 qe1 44.192 k 1 0.117 Radj 2 0.994 qe2 45.927 k 2 0.006 Radj2 1.000 59.622 71.648 58.320 69.575 0.140 0.148 0.998 0.996 59.920 71.437 0.007 0.008 0.998 0.999 82.165 91.253 81.541 90.117 0.170 0.193 0.999 0.998 82.879 91.523 0.009 0.010 0.999 0.996 104.201 102.148 0.174 0.996 104.321 0.010 1.000 Radj2 value, which is close to 1 for the Pseudo-second order. Moreover, the predicted adsorption capacity based on the Pseudo second-order model (qe2) shows a value close to the adsorption capacity of the ex- perimental results (qe (exp)). Temperature variations also appear to af- fect the adsorption, where an increase in temperature allows adsorption to occur faster and more favorable. 3.6. Root growth in Pi media A.thaliana was used as the model plant to assess the applicability of Pi-loaded composites as Pi-supplementation for plant growth. One of the most apparent phenotypical adaptive response in Pi-starved plant is displayed

4**by the suppression of the primary root growth**

along with the Fig. 7. Phosphate (Pi) adsorption kinetics data (C0 = 200 mg/L, T = 303, 313, 323 K) and fitting of: (a) acid-activated bentonite (AAB) at pH of 6, and (b) organo- bentonite (OrB) at pH of 8. Fig. 8.

1 Growth observation of Arabidopsis thaliana 10 days old **seedlings grown on** various **media. (a**) Images **of** 10 days **old seedlings. (b**

)

1 Primary root length of the seedlings

. From left to right: normal media (P+), phosphate-starved media (P-), Pi@AAB-supplemented phosphate-starved media (Pi@AAB), Pi@ OrB-supplemented phosphate-starved media (Pi@OrB), commer- cial fertilizer (Hyponex), and half dose of Pi@AAB and Pi@OrB. Different letters indicate a significant difference with $p < 0.05$. promotion of lateral root and root hair growth (Angkawijaya et al., 2017; Bernardo et al., 2018; Péret et al., 2011). To observe the root growth, A. thaliana seeds were grown on control media (P + and P—), bentonite-supplemented media for 10 days. To even up the amount of Pi source in bentonite-supplemented media, 84 mg Pi@AAB and 66 mg Pi@OrB were added to 50 mL phosphate-free media. As presented in Fig. 8, the seedlings grown on Pi@AAB had longer roots than P— seedling and were very slightly shorter than the one grown on P + . In contrast, the supplementation of full dose Pi@OrB (66 mg) caused severe growth retardation in root as well as aerial tissue, which shows pale green leaves. These impaired growths might be due to the presence of surfactant (i.e., rarasaponin) in excess, thus adversely affect seed germination, root growth, and overall plant biomass (Gálvez et al., 2019; Parr and Norman, 1964). The oc- currence of 1.32 g L−1 rarasaponin in Pi@OrB media is more than 2- fold higher than the recommended surfactant usage for the plant (< 0.65 g L−1) (Gálvez et al., 2019). To comply with the recommended surfactant concentration, media with half dosage of Pi@OrB were prepared. Interestingly, at a half dosage of Pi@OrB supplementation, the primary root length of the seedlings was significantly longer than the one grown on P- media and showed partial complementation of primary root growth. Thus confirm the toxic effect of excessive sur- factant (here rarasaponin) to the A.thaliana growth. In this work, commercial fertilizer (Hyponex N:P:K 10:30:20) was used to evaluate the applicability of Pi@AAB and Pi@OrB as plant fertilizer. As dis- played in Fig. 8, full- and half-dose Pi@AAB showed a comparable growth as the one grown on Hyponex-containing media. Pi@OrB sup- plementation showed more defect root growth compared to Pi@AAB; however, root lengthening in Pi@OrB-supplemented media (especially at ½ dose) was better than the one grown on P- media. 4. Conclusion Organo-bentonite (OrB) was prepared by modifying bentonite with rarasaponin-surfactant and chitosan. The current study demonstrates that OrB is a potential adsorbent for the removal of phosphate compounds (Pi) from aqueous solutions. OrB has higher adsorption capacity towards Pi compared to acid-activated bentonite (AAB). pH slightly affected the adsorption of Pi

6 onto AAB and OrB. **Adsorption isotherms of** Pi **on AAB and**

OrB were investigated and modeled using several isotherm models. The investigated adsorption systems show

6 a good fitting **with the Langmuir model**. Analysis of **the**

parameters of the other isotherm models shows conformity with the Langmuir model. Adsorption kinetics study reveals a rapid Pi removal at the beginning implies that the adsorption is driven by electrostatic force and sup- ported by the physical adsorption. A good fitting of kinetics data to Pseudo-second order models shows that the adsorption rate is a com- plex function of initial adsorbate concentration. Pi@AAB, at full- and

half- dose, can be used as Pi source to promote the primary root elon- gation of Arabidopsis thaliana. A full-dose Pi@OrB was shown to sup- press the primary root elongation, but, a half-dose Pi@OrB can promote root elongation better than the Pi-starvation media. These findings confirm the applicability of Pi@AAB and Pi@OrB as Pi supplements; however, the effect of supplementation on the actual soil can be dif- ferent. There are many factors in the actual soil (i.e., pH, humidity, organic matters, micro- and macronutrient content) that affect plant growth. Thus, more comprehensive studies are needed to examine the effects of the materials supplementation on the soil.

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Hazardous Materials 399 (2020) 123130

2**A.E. Angkawijaya, et al**. Journal **of**

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Hazardous Materials 399 (2020) 123130 2 3 4 5 6 7 8 9 10 11