



Sorption of Phosphate onto Surfactant-Modified Zeolite Particles

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Abstract

Slow-release phosphorous (P) fertilizer is basically considered as an approach to increase the efficiency of P fertilization on agricultural lands. This study aimed to examine the effect of pH solutions (3.5, 7, 9 and 11), contact times (10, 15, 30, 60, 90, 120 and 150 minutes), and solid-solution ratios (1:500, 1:1000, and 1:1500) on the capability of zeolite as a material for the development of slow-release fertilizers for absorbing phosphate ions. The surface of natural zeolite was chemically modified through surfactant addition (hexadecyltrimethylammonium bromide - C₉H₄₂BrN or HDTMABr), and the capability of surfactant-modified zeolite (SMZ) to adsorb phosphate ions was studied through batch experiments. Results of the study showed that pH solution affected the sorption of phosphate ions onto SMZ, in which pH solution of 5.0 showed high P adsorption and was below the p*H*_{pzc} of SMZ. The amount of adsorbed P onto SMZ does not vary based on changes in contact time.

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Result of the study also revealed that the maximum sorption capacity (Q_{\max}) of phosphate ions onto SMZ increases with increasing solid-solution ratios. Results of this study show that SMZ may potentially be used as an material for the development of slow-release P fertilizers, in which the pH solution and solid-solution ratio control the amount of sorbed P onto SMZ.

Keywords: desorption; Langmuir isotherm; surface charges; substitute isomorphous; ionic bonding.

1. Introduction

Elemental phosphorous (P) is one of the essential nutrients for plants and is required in large quantities to maintain profitable crop yields. Since the P contents are generally low in soils [1, 2], P fertilization is carried out to meet the P nutrient requirements for plants. The efficiency of P fertilization on agricultural soils is generally very low, only around 1.0-2.50% of the total P in the soil is immediately available for plant uptake [3]. Most of P ions from fertilizers are chemically fixed by Fe and Al in acid soils and by Ca and Mg in alkaline soils, so they are present in the form that is not available for plant uptake to support plant growth [4, 5]. Some of the P ions from fertilizers are lost from the root zone through the leaching process and will be transported through the water stream, which in turn may cause eutrophication in the water body [6-8]. Results of these studies show the importance of nutrient P management in the soils to increase the efficiency of P fertilization in agricultural soils.

Several technologies have been developed to increase the efficiency of P fertilization in agricultural soils. For example, the development of water soluble phosphate products, such as triple superphosphate (TSP), makes soil solution P more available to plant uptake shortly after fertilizer application to soils [9]. The application of soil biotechnology such as mycorrhizae and phosphate solubilizing microbes are reported to be able to increase the efficiency of phosphate uptake and crop production [10-12]. However, these technologies do not solve the problem of the amount of phosphate provided by fertilizers sufficient for plant demand at each stage of growth.

One methodology being comprehensively studied to increase phosphorous use efficiency is to provide a barrier in order to reduce the rate of phosphate ion release from fertilizers to soil solutions. This can be achieved by increasing the strength of phosphate sorption onto colloidal surface, which result in phosphate will have a longer time to be transported from the surface to soil solutions [13]. Increasing stability will not only reduce the concentration of phosphate in soil solution but will also slow the rate at which the nutrient is resupplied once depleted [14]. Therefore, the development of products that slowly release P over the course of the growing season will be able to meet P nutrient requirements in accordance with crop demand. The approach to reduce phosphate release from fertilizers to soil solutions consisted of coatings, scaffolds, organic matrices, and minerals of limited solubility [9].

Zeolite is one of the materials frequently used for the development of slow P fertilizers. Zeolite is the aluminosilicate members of the family of microporous solids known as molecular sieves, and mainly consists of silicon, aluminum and oxygen [15, 16], and has a net negative charge [17, 18]. Modification of zeolite surface has been conducted to make zeolite has the capability to adsorb anionic ions and waste. The modification could be achieved by surfactant addition such as hexadecyltrimethylammonium-bromide (HDTMABr) to zeolite [19,

20]. Several previous studies showed that surfactant-modified zeolites (SMZ) had higher phosphate adsorption compared to the natural zeolite [21-23]. Results of these studies suggest that SMZ has a high potential to be used as materials for the development of slow-release P fertilizers. Although there have been many studies on the use of SMZ as a material to enhance P sorption, information about the factors affecting the adsorption of P ions onto SMZ is still unclear. Previous study showed that the sorption of P ions onto SMZ is influenced by many factors [17, 24]; however, this research is limited only to examine the effect of environmental factors on P sorption. Therefore, this experiment aimed to quantify the effect pH solution, contact time, and solid-solution ratio on the sorption of phosphate onto SMZ.

2. Materials and Methods

2.1. Surface Modification of Zeolite

The zeolite used in this study is in the form of a conventionally milled powder and is generally applied to sewage treatment and other uses. This natural zeolite is obtained from Klaten Regency, Central Java Province, Indonesia. Natural zeolite is then processed into a smaller size using planetary ball milling where the zeolite is ground in wet conditions. The milling process is carried out for 24 hours using a ball size of 5.0 mm with a ball per ratio (BPR) of 1:50. The results of particle size analysis using the Particle Size Analyzer (Nanoplus/Particular System) showed that the zeolite had a particle size of $D_{50} = 709.1$ nm (Table 1). The results of X-ray diffraction (XRD) analysis showed that the types of minerals contained in zeolite consisted of 29.4% modernite, 13.2% Ca-clinoptilolite, 12.1% heulandite, 6.1% Ca-heulandite, and others 14.7%.

Table 1: Selected chemical properties of zeolite particles.

Properties	Values
Cation exchangeable capacity (cmol kg^{-1})	57.25
Specific surface areas ($\text{m}^2 \text{g}^{-1}$)	84.51
Diameter (D_{50}) (nm)	709.10
Zeta potential (mV)	-79.39
SiO ₂ (%)	60.73
Al ₂ O ₃ (%)	21.29
CaO (%)	7.41
Fe ₂ O ₃ (%)	5.20
P ₂ O ₅ (%)	1.05
K ₂ O (%)	1.34
MgO (%)	0.90
SiO ₂ /Al ₂ O ₃	2.85

Cation exchangeable capacity (CEC) of zeolite was determined using ammonium acetate (pH 7.0) method, and the result showed that the CEC of zeolite was $57.25 \text{ cmol kg}^{-1}$ (Table 1). Dominant elements in zeolite particles were estimated using X-Ray Fluorescent Spectroscopy (Torontech EDXpert Type Portable XRF Analyzer). Specific surface areas (SSA) of zeolite particles were determined by five-point nitrogen adsorption at 77 K and the subsequent desorption of nitrogen with an autosorb instrument (Nova 4200 Analyser, Quantachrome Corp., Boynton Beach, USA). Zeta potential of zeolite was quantified using Chemisorption Analyzer (Micromeritic Type AutoChem II 2920). Details of the elements, SSA, and zeta potential of zeolite particles are described in Table 1.

Modification of zeolite surface charges was carried out using hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$ or HDTMABr), in which 5 g of zeolite particles was mixed homogeneously with 125 mL of HDTMABr solution with a concentration of 2 times the CEC of zeolite. The mixture of zeolite particles and HDTMABr solution was shaken for 6 hours, and then filtered using Whatman Filter Paper No. 42. The solids on filter paper were dried in an oven at 80 °C for 24 hours. Absorption of HDTMABr surfactant on the zeolite surface was confirmed by fourier-transform infrared spectroscopy (FTIR) analysis that showed the presence of bands of 3042 cm^{-1} and 3383 cm^{-1} due to N-H stretching and band of 1619 cm^{-1} due to N-H bending (data of FTIR was not shown).

2.2. Experiment of Phosphate Sorption

Different pH solutions: 3, 5, 7, 9 and 11 (first preliminary experiment) and different contact times: 10, 15, 30, 60, 90, 120 and 150 minutes (second preliminary experiment) were performed to establish optimum equilibrium pH and contact time for phosphate adsorption onto SMZ. In the first experiment, 10 mg of SMZ was put into a 50 mL Erlenmeyer and 10 mL of a KH_2PO_4 solution with a concentration of 10 mg P L^{-1} was added to the Erlenmeyer, and then the pH solution according to the treatment was adjusted by adding 0.1 M HCl or 0.1 M NaOH. The mixed phosphate-SMZ was then shaken for 4 hours, and then filtered with Whatman Filter Paper No. 41. Next, 2 mL of the filtrate was pipetted and put into a test tube, a few drops of molybdovanadate reagent were added, and the concentration of phosphate in the filtrate was measured by a spectrophotometer at 400 nm. Details of the second preliminary experiment follow the first preliminary experiment with the exception of the contact times used are 10, 15, 30, 60, 90, 120 and 150 minutes. The amount of adsorbed P onto SMZ was calculated based on the difference in phosphate concentration in the solution before and after equilibrium.

Results of preliminary experiments showed that the optimal pH and time for phosphate adsorption onto SMZ were at pH 5.0 and 30 minutes, respectively. These pH solution and contact time were then employed to study the effect of solid-solution ratio on phosphate sorption onto SMZ. Different concentration of phosphate solutions: 0–75 mg P L^{-1} was added to 10 mg of SMZ in centrifuge tubes with different solid-solution ratios (1:500, 1:1000, and 1:1500). The pH solution was adjusted to 5.0 using 0.1 M HCl or 0.1 M NaOH then shaken for 30 minutes. The details of this experiment were similar to those of the preliminary implementation of the phosphate adsorption experiment. Phosphate sorption data was then fitted to the Langmuir equation using the least square curve fitting method in Microsoft Excel®.

3. Results and Discussion

3.1. Effect of Solution pH and Contact Time on Phosphate Sorption

The results showed that the amount of P adsorbed by SMZ varied based on the difference in pH of solution. The amount of P sorbed onto SMZ decreased with increasing pH of solution. The amounts of P sorbed onto SMZ reached to 3.65–3.70 mg P 100 g^{-1} at pH 3.00–7.00, reduced to 3.33–3.40 mg P 100 g^{-1} when the solution pH increased to 9.00–11.00 (Figure 1). Changes in the amount of adsorbed P with changes in solution pH were also reported in several previous studies. For example, He and his colleagues [25] incorporated lanthanum oxide onto zeolite and found that lanthanum-modified zeolite would effectively adsorb phosphate over pH range of

3.0–7.0, while alkaline conditions were unfavorable for phosphate sorption. In another study, Guaya and his colleagues [26] reported that the lowest phosphate sorption onto hydrated aluminium oxide-modified zeolite occurs at pH below than 2.00, and the highest with a plateau between pH 3.00 and 6.00 to decreases then from pH 6.00 to 11.00. Results of those studies show the importance of solution pH on control the sorption of phosphate onto modified natural zeolite.

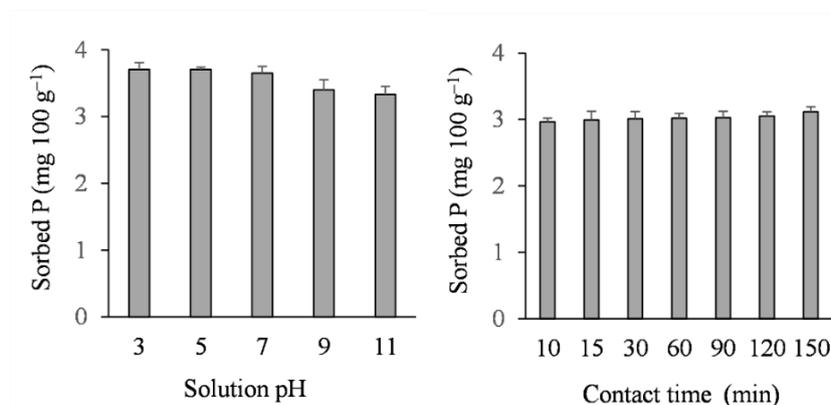


Figure 1: Effect of solution pH (left) and contact time (right) on P sorption onto surfactant-modified zeolite particles. Lines above the bars indicate the standard deviation of mean (n=3).

The sorption of phosphate ions (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) onto SMZ is related to anion exchange between Br^- originating from HDTMA-Br impregnated on the SMZ and phosphate ions [20, 27-29]. The amounts of sorbed P onto SMZ is controlled by pH_{pzc} (point zero of charges) of SMZ. Several studies show that the PZC of SMZ is observed at pH range of 6.25–8.00 [30, 31]. At pH levels between 3.00 and 5.00 (which is the pH used in this study), the surface charge of SMZ was positive and appropriate for the attraction of anions through electrostatic forces. At pH above the pH_{pzc} , the surface charge of SMZ was negative, and this resulted in decreasing the sorption of phosphate ions. Results of this study demonstrate that the PZC of SMZ play an important mechanism in the sorption of phosphate ions onto SMZ. At pH higher than pH_{pzc} in which the SMZ has negative charges, other mechanisms may be responsible for the sorption of phosphate ions onto SMZ. These mechanisms include: 1) interaction of the anions by the hydrated cations of zeolite through hydrogen bonding, 2) substitution of anions with OH bonded to Al or Si atoms, 3) attraction or substitution of anions onto the partial protonated sites of OH_2^+ and 4) occlusion mechanism [32, 33]. Solution pH also determines chemical forms of inorganic phosphate. At solution pH is less than 2.0, phosphate presents as H_3PO_4 , at pH between 3.0 and 6.5 the dominant chemical form is H_2PO_4^- , HPO_4^{2-} dominates at pH between 7.5 and 12.0, and P exists as PO_4^{3-} when pH exceeds 12.0 [34]. Consequently, when the pH of the equilibrium solution was alkaline (pH 9.0–11.0), P was mostly in the divalent form of HPO_4^{2-} , and this may result in decrease in P sorption [26]. Therefore, solution pH of 5.00 is selected for next experiments based on the results of the study and the pH_{pzc} of SMZ.

The influence of contact time on the P sorption onto SMZ is illustrated in Figure 1. The results showed that the increase in contact time from 10 min to 150 min did not result in increasing the amounts of sorbed P onto SMZ,

in which the P sorption was relatively constant at 2.96–3.11 mg P 100 g⁻¹ regardless the differences in contact time. Similar results are reported by Nekhunguni and his colleagues [35] who found that the sorption of uranium (VI) onto modified zeolite did not change after 30 min. The rapid adsorption of phosphate ions may occur in the initial stage could be due to the higher concentration gradient and more available vacant sites for adsorption. Nekhunguni and his colleagues [35] reported that adsorption capacity of uranium (VI) increased abruptly from 0.038 to 0.14 mg g⁻¹ as the time increased from 0.5 to 30 min. However, results of this study was different to those obtained by Hailu and his colleagues [36] who observed that contact time of 6 h and 24 h results in 91.8% and 83.8% removal of acid blue dye and Cr(VI), respectively. Longer contact time may allow higher sorption onto modified zeolite.

3.2. Effect of Solid-Solution Ratios on Phosphate Sorption

The addition of hexadecyltrimethylammonium-bromide (HDTMA-Br) leads to the creation of the anionic adsorption site on the surface of zeolite. During the modification stage, HDTMA⁺ cations attract by columbic bonds on the negative surface of zeolite and result in changes in monolayer coverage of zeolite to bilayer coverage of zeolite. The size of the HDTMA⁺ ions is too large to enter the zeolite channels. Thus, the bilayer of HDTMA⁺ (adsorption sites) is formed on the external surfaces of zeolite; since the film diffusion and anion exchange rates are the rate limiting factors [31]. This mechanism leads to changes in zeta potential of particles from negative to positive and great enhancement of the P-adsorption capacity [37].

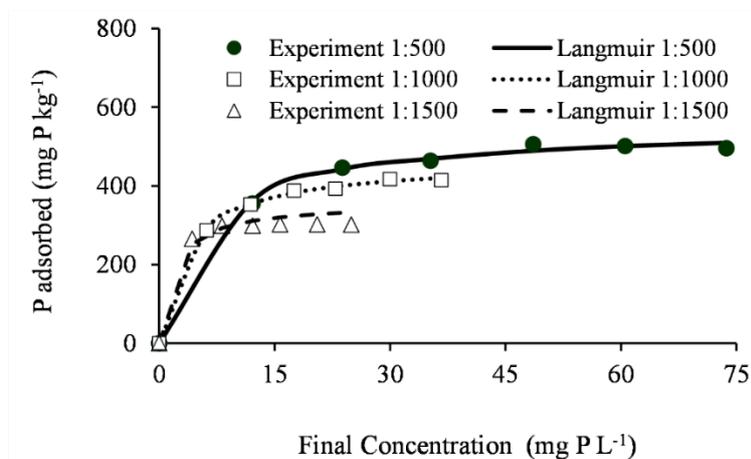


Figure 2: Isotherms (experimental and Langmuir) of P adsorption onto surfactant-modified zeolite particles at three different solid-solution ratios.

Sorption isotherms for phosphate ions on SMZ with different solid-solution ratios are shown in Figure 2. The sorption isotherms could be modelled reasonably well using the Langmuir equation, with r^2 values ranging between 0.97 and 0.99 (Table 2). On a study of phosphate sorption onto hydrated aluminum oxide-modified natural zeolite, Guaya and his colleagues [26] fit the experimental data to the Langmuir and Freundlich isotherm, and they reported that phosphate sorption data are well described by the Langmuir isotherm while Freundlich isotherm provides a good description only at the lower concentration ranges. Several previous studies showed that the Langmuir model has a good prediction of experimental data of phosphate and other

anion sorption onto the surface of modified zeolite [27, 31, 38].

Table 2: Langmuir equation isotherms for phosphate sorption onto surfactant-modified zeolite particles with different solid-solution ratios. Numbers in parentheses represents the standard deviations of mean (n=3).

Solid-solution ratios	Q_{\max} (mg kg ⁻¹)	K (L mg ⁻¹)	r^2
1 : 500	554.59 (7.05)	0.156 (0.007)	0.99
1 : 1000	462.70 (50.71)	0.270 (0.005)	0.99
1 : 1500	356.35 (58.70)	0.568 (0.011)	0.97

The results showed that the maximum sorption capacity (Q_{\max}) of SMZ for phosphate sorption was in the range of 356–555 mg kg⁻¹, depending on the ratios of solid–solution (Table 2). The Q_{\max} value obtained in this study was in the range of Q_{\max} values for phosphate sorption onto modified-zeolite in previous studies. The Q_{\max} value in this study was higher than that in the study conducted by Gao and his colleagues [39] who reported that the maximum sorption capacity of phosphate ions onto iron-modified zeolite varied from 108 to 186 mg kg⁻¹. However, the value of Q_{\max} in this study was lower than that reported by Feng and his colleagues [40] who found the maximum sorption capacity of phosphate sorption onto Mn-, Fe-, and Zr-modified zeolite was in the range of 5–20 mg g⁻¹. The ability of modified–zeolite to adsorb phosphate was related to the materials to be added to the zeolite during the modification process. Q_{\max} value of Lanthanum–modified zeolite reached to 52 mg g⁻¹ [38], 32 mg g⁻¹ of chitosan–modified zeolite [41], and 25–58 mg g⁻¹ of synthetic zeolites obtained from fly ash and modified with lanthanum [42]. The results of these studies show that the ability of modified-zeolite particles to absorb phosphate is largely determined by changes in the chemical properties of the zeolite surface that occur during the modification process.

The results showed that increasing solid-solution ratios (SSR) increased adsorption of phosphate ions onto SMZ (Figure 2). Increasing the solid-solution ratio from 1:1500 to 1:500 resulted in improvement in the maximum sorption capacity (Q_{\max}) of phosphate onto SMZ from 365 from 365 mg P kg⁻¹ to 555 mg P kg⁻¹ (Table 2). The increase in the value of Q_{\max} is related to the increasing concentration of P solution in the phosphate ions-SMZ system, which has implications for the increasing opportunity for phosphate ions to be adsorbed on the SMZ surface.

Previous studies have shown different responses of anions adsorption on mineral surfaces to changes in SSR. Adsorption isotherm is theoretically dependent on the SSR, in which the adsorption of U(VI) to Fe(III)-containing materials increases with an increase in solid-solution ratio [43]. Similar results are also reported by Cheng and his colleagues [44] who found that uranium (VI) sorption onto goethite-coated sand increases with increasing SSR ranging from 33.3 to 333 g L⁻¹. However, SSR did not influence the rate of arsenic (As) sorption onto drinking-water treatment residual [45] and the amount of phosphate sorbed onto fresh water sediment [46]. In fact, some studies show that a decrease in SSR lead to increases in the sorption of anions onto minerals. For example, amounts of sorbed atrazine and simazine onto biochar increased from 451 to 1158 mg kg⁻¹ and 243 to 1066 mg kg⁻¹, respectively, when the SSR decreased from 1:50 to 1:1000 (g mL⁻¹) [47]. In another study, Zhou and his colleagues [48] showed that As(V) sorption by FeS decreased with increased in

SSR. Results of these studies show different effects of SSR on the sorption of anions

4. Conclusion

Solution pH plays a very significant role in the ability of surfactant-modified zeolite particles in phosphate sorption. The role of solution pH in phosphate sorption is fundamentally dependent on the pH for point zero of charge of surfactant-modified zeolite particles and dominant species of phosphate ions in the solution. The results also show that different contact time does not influence the amounts of sorbed phosphate ions on surfactant modified zeolite particles. Phosphate sorption onto surfactant modified zeolite particles could be modelled reasonably well using the Langmuir isotherm. The maximum sorption capacity of phosphate ions onto the surfactant-modified zeolite particles increases with increasing solid-solution ratio. The result of the study demonstrates that surfactant-modified zeolite particles have the ability to adsorb phosphate ions, in which the amounts of sorbed onto the particles is controlled by solution pH and the solid-solution ratio.

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