Jurnal Akademika Kimia, 11(2): 83-90, May 2021
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.fkip.untad.ac.id/index.php/jak/

OPEN ACCESS

Phospate Release Study on Silica Gel and Amino Silica Hybrid Sorbent from Lapindo Mud

***Ade I. Agipa[1] & Muhamad F. Muarif[2]**
[1]Program Studi Biologi/FSains – UIN Sultan Maulana Hasanuddin, Banten – Indonesia 42118
[2]Program Studi Fisika/FSains – UIN Sultan Maulana Hasanuddin, Banten – Indonesia 42118
Received 10 March 2022, Revised 21 April 2022, Accepted 09 May 2022
doi: 10.22487/j24775185.2022.v11.i2.pp83-90

Abstract

This study discusses the rate of phosphate release in Silica Gel (SG) and Amino Silica Hybrid (ASH) sorbents using Lagergren pseudo-first order kinetic and Lagergren Pseudo-second order kinetic. ASH synthesis was done by adding a 3-aminopropyltriethoxysilane (APTES) modifier to sodium silicate from Lapindo Mud. Phosphate binding was carried out at 30 minutes with a stirring speed of 250 rpm. Analysis using IR spectrophotometer showed the success of ASH synthesis as indicated by the appearance of functional groups -NH_2 and -CH_2 at wavenumbers 1635 cm^{-1} and 1473 cm^{-1}. With the continuous method, SG and ASH sorbents that have bound phosphate were then desorbed at various times of 2, 3, 4, 7, 8, and 9 days. The amount of phosphate anion released from SG and ASH was tested using a UV-Vis instrument then modeling was carried out to determine the rate of phosphate release. The desorption results showed the amount of phosphate released from the ASH sorbent was less than that of the SG sorbent. Through modeling, the proceeds of the phosphate release rate follow the Lagergren Pseudo-second Order Kinetic with an experimental QE of 0.22089 M/g for SG sorbent and 0.33333 M/g for ASH sorbent.

Keywords: Lapindo mud, silica gel, amino silica hybrid, 3-aminopropyltriethoxysilane (APTES)

Introduction

Lapindo Mud contains silica (SiO_2), as much as 50%, which can be used as a primary material in synthesizing Silica Gel (SG) by adding an alkaline base to form metal silicates. Rahmayanti et al. (2020) compared the product yields obtained from silica extraction using NaOH and KOH bases at various reaction times. With the addition of acid with the same concentration, the result of silica was obtained, which was higher in silica extraction using NaOH base with a reaction time of 4 hours.

According to Buhani et al. (2009), the higher the base concentration, the more silica is extracted. SG is used as an adsorbent due to its inert, neutral properties, large surface area, large adsorption capacity, and active surface sites in silanol groups (-Si-OH). Siloxane groups (-Si-O-Si) allow it to adsorb adsorbate whether it is a metal, anion, or cation. Besides being used as an adsorbent, SG also has a weakness in silica gel's low effectiveness and selectivity. The oxygen atoms in the silanol (-Si-OH) and siloxane (-Si-O-Si) groups have small sizes and polarizability, so it is difficult to bond with giant and large polarizability metals. The surface modification of silica gel, which aims to add surface-active groups, can be done by impregnation or forming covalent bonds. Modifying covalent bonds can be done by adding modifiers in organofunctional or functional inorganic compounds. 3-aminopropyltriethoxesilan (APTES) is one of the solutions used to add amino groups, amino-functional groups, or -NH_2 (Ikhsan et al., 2018).

The surface modification of silica gel, which aims to add surface-active groups, can be done by impregnation and sol-gel methods. Using the sol-gel process, adding a modifier in an organofunctional or a functional inorganic compound to the silica precursor produces amino silica hybrid (ASH). The substitution of the silanol group with the active group in the modifier forms covalent bonds. One of the modifiers that can add an amino-functional group or -NH_2 is APTES (Ikhsan et al., 2018). In the synthesis of amino-modified silica, the grafting of amino groups is carried out simultaneously with the formation of SG.

Phosphorus is an essential nutrient that plants need for growth. Plants absorb phosphorus from inorganic ions and quickly turn it into organic compounds. This phosphorus is mobile or easy to move between plant tissues. The optimal concentration of phosphorus in plants during vegetative growth is 0.3% - 0.5% of the dry weight of the plant. Phosphorus must be given to plants in the right amount. Excess phosphorus can cause the

growth of plankton and aquatic plants to be significant. In addition, extra phosphorus in the form of phosphate is also responsible for eutrophication in lakes (Chen et al., 2015; Maslukah et al., 2020). According to Braun et al. (2022), excessive use of phosphate fertilizers can cause half of the arable land in Sweden to become unstable.

Phosphate release rate in SG and ASH sorbent was studied through desorption kinetics. ASH has solid covalent bonds to absorb phosphate anions contained in fertilizers. The strong bond causes the phosphate to desorb for a long time, so it does not cause the soil to become saturated. The desorption rate of the phosphate anion is low, so it can be used as a candidate for making slow release fertilizer (SRF) (Gypser & Freese, 2020).

Methods

Materials

The equipment used in this research included glassware, pH meter, thermometer, oven, furnace, magnetic stirrer with hotplate, Teflon, analytical balance OHAUS Paj 10003, 200 mesh and 100 mesh sieves, 1 set of Buchner filter, FTIR-Shimadzhu 8201 spectrophotometer. PC, and UV Vis spectrophotometer type UV-2400PC Series.

The materials used in this study were Lapindo Mud, 1 M HCl, 3 M NaOH, 3-Aminopropyltriethoxysilane (APTES), KH_2PO_4 as a P source, Molybdate Complex, and demineralized water.

Synthesis of sodium silicate

Lapindo Mud dried at 100 °C for 1 hour and continued calcination at a temperature of 900 for one hour. A total of 10 grams of calcined Lapindo Mud (200 mesh) was put into Teflon, then 100 mL of 3 M NaOH solution was added. The mixture was heated at a temperature of 98 °C for one hour. The sodium silicate filtrate was obtained by filtering the mixture with Whatman filter paper. 42.

Synthesis of silica gel the

Sodium silicate filtrate was added slowly with 1 M HCl until it reached pH 7 and formed a white residue. Silica Gel residue was washed with demineralized water and dried at a temperature of 80 °C until dry.

Synthesis of amino silica hybrid

APTES as much as 4 mL was put into sodium silicate solution and 1 M HCl was added slowly to pH 7, and a white precipitate was formed. The Amino Silica Hybrid residue was washed with demineralized water and dried at 80 °C until dry.

Phosphate binding on the variation of contact time

1.5 grams of SG was put into 150 mL of 0.01 M KH_2PO_4 solution and then stirred at 250 rpm. A total of 10 mL of sample was taken at a contact time of 30 minutes. SG, which has bound phosphate, is then centrifuged. A total of 1 mL of filtrate was added with 3 mL of molybdate complexing and was diluted to a volume of 10 mL and then analyzed by UV Vis as the concentration of residual phosphate. The difference in initial and residual phosphate concentrations is the amount of phosphate bound by SG. Treatment was carried out for the ASH samples.

Release of phosphate on the variation of contact time

A total of 1.5 grams of SG, which had bound phosphate, was put into 150 mL of aqua DM at pH 3 then the sample was stirred using a stirrer during the variation of the release time. Then 10 ml of the sample was centrifuged, and the filtrate was analyzed. A total of 1 mL of filtrate was added with 3 mL of molybdate complexing and was diluted to a volume of 10 mL and then analyzed by UV Vis as the concentration of residual phosphate. The test was continued at time variations of 2, 3, 4, 7, 8, and 9 days. Treatment was performed for the ASH sample.

Results and Discussion

Lapindo mud contains 50% SiO_2, which can be synthesized into SG. The content of lapinda mud can be seen in **Table 1**

The lapindo mud was prepared by calcining at 900 °C for 1 hour (Zaemi et al., 2013). The heating of the Lapindo Mud at a high temperature was carried out to remove the organic fraction from the Lapindo Mud so that only the inorganic fraction was left.

Silica from lapindo mud is extracted by adding an alkaline solution (in this case, NaOH) and reacted at a 95-105 °C to form a sodium silicate solution. Sodium silicate can be synthesized using an alkaline solution and reach a relatively low temperature of 95-105°C. This sodium silicate solution is a precursor for manufacturing SG and ASH (Sriyanti et al., 2005). The reaction for the formation of silica can be seen in the equation (1), (2), and (3):

$$SiO_2(s)+2NaOH(aq)\rightarrow Na_2SiO_3(aq)+H_2O(l) \quad (1)$$

$$Na_2SiO_3(aq)+2HCl(aq)\rightarrow 2NaCl(aq)+H_2SiO_3(aq) \quad (2)$$

$$H_2SiO_3(aq) + H_2O(l)\rightarrow Si(OH)_4(aq) \quad (3)$$

Table 1. Composition of lapindo mud (Rahmayanti et al., 2020)

Compound	Concentration (%)
SiO_2	50.00
Al_2O_3	6.00
SO_3	1.60
K_2O	2.46
CaO	8.59
TiO_2	2.02
V_2O_5	0.10
MnO	0.44
Fe_2O_3	27.70
CuO	0.14
ZnO	0.05
Br	0.08
Rb_2O	0.04
SrO	0.49
ZrO_2	0.10
Re_2O_7	0.07

The synthesis of SG and ASH was synthesized by adding mineral acid to a sodium silicate solution until the pH of the solution was neutral (Sdiri et al., 2014). During the reaction, there was a very rapid decrease in pH 9 - 7, accompanied by gel formation. The addition of acid continuously will cause the gel formed to dissolve again due to the trapping of Na metal ions in the gel matrix and cannot be dissolved by washing. The SG is left overnight for the aging process, followed by the washing process. The washing SG with demineralized water neutralizes NaCl and forms $Si(OH)_4$ orthosilicic acid sol. Furthermore, the orthosilicic acid sol of $Si(OH)_4$ undergoes a hydrolysis reaction to form SG.

Adding hydrochloric acid to sodium silicate causes protonation of the silicate anion to become silanol which then reacts again with the silicate anion to form siloxane (Sriyanti et al., 2005). The reaction continues until silica is formed. The synthesis of ASH was carried out using the sol-gel method by adding APTES to a sodium silicate solution, a silica precursor. The formation of the amino silica hybrid begins with the protonation of the ethoxy group's oxygen atom (O) (-OCH_2CH_3) in the organic compound APTES due to the addition of acid. Furthermore, the silicate anion species (Si-O-) plays a role in attacking the –Si- atom in APTES, where the O atom in the ethoxy group has been protonated. The incoming silicate anion species will replace the ethoxy group –OCH_2CH_3 with a protonated O atom to form a siloxane bond. The ethoxy group with protonated O atom will be released in the form of ethanol. The continued addition of acid causes the reaction to continue until all the ethoxy groups in the APTES ligand undergo a silicate anion species condensation reaction by releasing ethanol (Ikhsan et al., 2018). The success of the synthesis of SG and ASH can be seen in **Figure 1.**

The results of the IR spectra analysis on the SG sample showed the appearance of stretching vibrations of the –OH group from –Si-OH at a wavenumber of 3448 cm^{-1}, asymmetric stretching vibrations -Si–O from Si–O–Si at a wavenumber of 1095 cm^{-1}, stretching vibrations Si-O symmetry of --Si-O-Si- at wavenumber 794 cm^{-1}, bending vibration of –OH group from –Si-OH at wavenumber 1635 cm^{-1}. Modification by adding APTES to the ASH synthesis showed the appearance of amides at an absorption wavenumber of 2939 cm^{-1}, which corresponds to the asymmetric stretching vibration of ≡C–H. The amide absorption at a wavenumber of 1527 cm^{-1} is identical to the combination of the C–N stretching vibration with the -NH deformation of the peptide group. The amide absorption at a wavenumber of 1242 cm^{-1} shows a combination of C–N stretching vibrations and deformation of the amide bond arising from vibrational vibrations of the CH_2 (Swasdika et al., 2021).

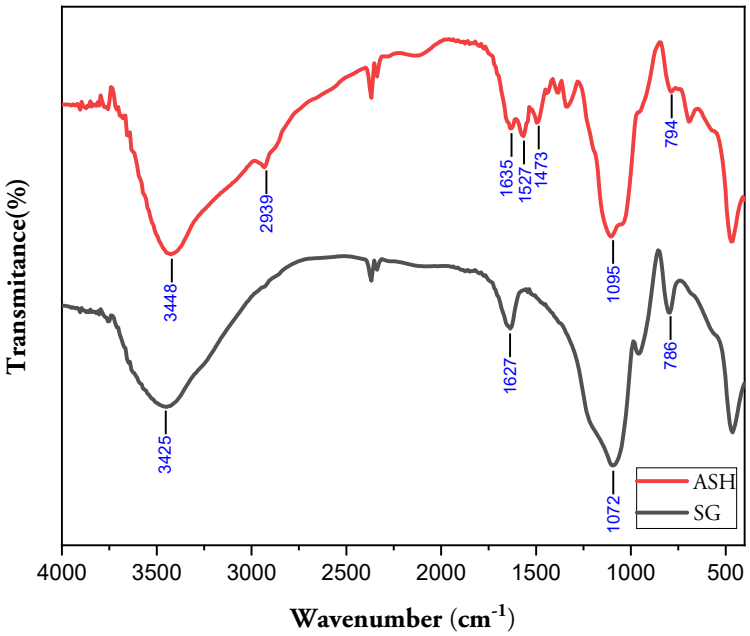

Figure 1. FTIR spectra of SG and ASH

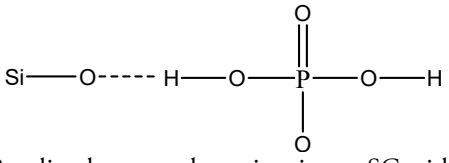

Figure 2. Bonding between the active site on SG with phosphate

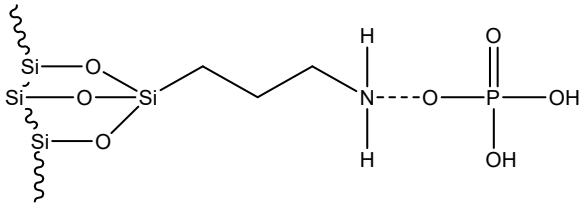

Figure 3. Bonding between the active site on ASH with phosphate

Adsorption of phosphate with SG and ASH was carried out within a concentration of phosphate 0,01 M, time of 30 minutes, and the reaction pH being 5, referring to research conducted by Ikhsan et al. (2018) to obtain the optimum conditions for the phosphate-binding reaction. SG and ASH bind to phosphate following the Langmuir isotherm pattern, monolayer (Saki et al., 2020; Jalali & Peikam, 2013). The continuous addition of phosphate will not affect the increase in the amount adsorbed because the active site is filled (Buhani & Suharso, 2010). **Figures 2** and **3** show phosphate binding to SG and ASH. Phosphate binding with SG occurs because of the interaction between the O atom derived from the phosphate with the silanol active site. In amino-modified silica, the phosphate bonded to the ASH sorbent through a bond between the O atom from the phosphate and the N atom from the amino group.

Through adsorption experiments, the results obtained that the concentration of phosphate bound to the SG sorbent was 0.0021 M and the ASH sorbent was 0.00325 M. An increase in the amount of phosphate attached to the ASH sorbent was due to the rise in the active amino sites (Kondalkar et al., 2018). The SG and ASH sorbent, which had bound phosphate, were then subjected to desorption experiments at variations in contact time of 2, 3, 4, 7, 8, and 9 days. **Table 2** is the data of phosphate released at variations in contact time.

Table 2. Percentage phosphate release from SG and AHS

Time (days)	SG			ASH		
	Absorbance	Concentration release	% release	Absorbance	Concentration release	% release
2	0.032	0.00032	18.14	0.052	0.00052	14.96
3	0.029	0.00029	15.29	0.038	0.00038	10.13
4	0.029	0.00029	14.19	0.032	0.00032	7.88
7	0.027	0.00027	12.17	0.034	0.00034	7.74
8	0.028	0.00028	11.58	0.039	0.00039	8.17
9	0.027	0.00027	10.14	0.037	0.00037	7.04

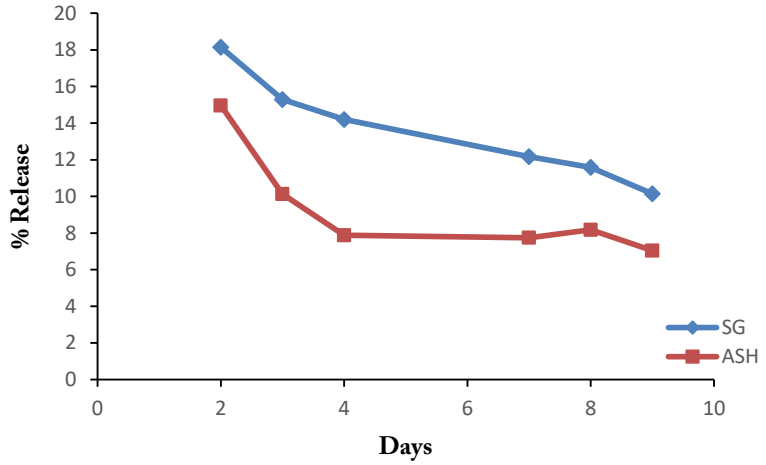

Figure 4. Phosphate release by SG and ASH sorbent

Table 2 shows the percentage of the amount of phosphate released from the adsorbent SG and ASH. The data above shows decreased desorbed phosphate with increasing time (Audette et al., 2016; Yang et al., 2019). On the second day, the phosphate released from the SG sorbent was 18.14%, and the ASH sorbent was 14.96%. Over time, the percentage of phosphate released from the SG and HAS sorbents decreased. On the ninth day of desorption, the phosphate released was reduced to 10.14% for the SG sorbent and 7.04% for the ASH sorbent. The amount of phosphate released was smaller in the ASH sorbent than in the SG sorbent. The amino group modification causes the formed covalent bonds to become stronger.

Phosphate desorbed from the ASH sorbent is smaller than the SG sorbent. The active silanol group has been modified using an amino group to strengthen the covalent bond in the ASH sorbent. It indicates that the phosphate and adsorbent ASH bond is more potent than SG. In the ASH adsorbent, the number of active sites that bind phosphate is influenced by the silanol and siloxane groups, but the presence of amino groups from the addition of the APTES modifier so that less phosphate is desorbed. The relationship between time vs. phosphate released from SG and ASH sorbents can be seen in **Figure 4**.

The reaction order and rate constant can be determined by modeling Lagergren pseudo-first order kinetic and Lagergren pseudo-second order kinetic.

Equation (4) shows Lagergren pseudo-first order kinetic, while equation (5) shows Lagergren Pseudo-second order kinetic

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2{,}303} t \quad (4)$$

$$\frac{1}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (5)$$

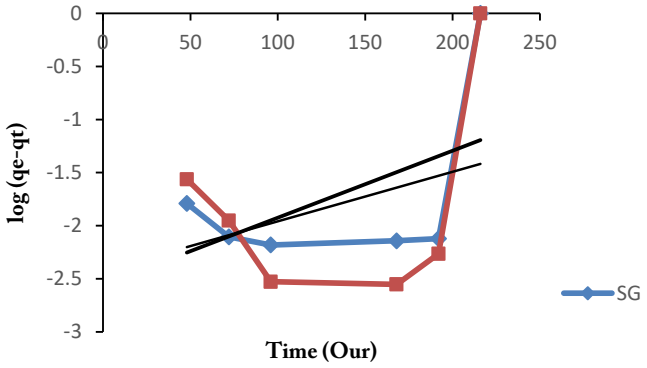

Figure 5. Pseudo-first order reaction of desorption phosphate by SG and ASH

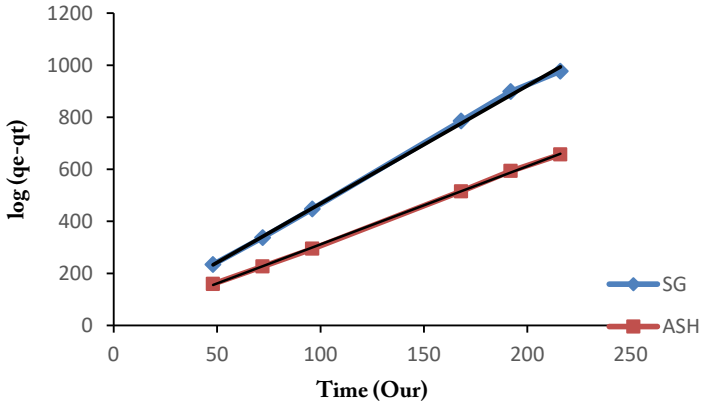

Figure 6. Pseudo-second order reaction of desorption phosphate by SG and ASH

Figure 5 shows Lagergren's kinetic modeling Pseudo-first Order Kinetic created by plotting time vs. log (QE-qt). Based on the Lagergren pseudo-first Order Kinetic on SG and ASH, it produces a linear equation Y=0.006x - 2.556 with a determinant coefficient value of 0.259 for SG and Y= 0.004x - 2.426 with a determinant coefficient of 0.112 on ASH. Phosphate release rates for SG and ASH have relatively small determinant coefficients, so Lagergren Pseudo-second order kinetics modeling was carried out.

Figure 6 shows Lagergren's kinetic modeling Pseudo-second order kinetic is made by plotting time vs. t/qt to produce a linear equation Y= 4.527x + 15.79 with a coefficient of 0.998 for SG and Y= 3,000x + 11.38 with a determinant coefficient of 0.999. Based on the kinetics modeling, it is known that the desorption of phosphate from the adsorbent SG and ASH follows the Lagergren Pseudo-second order kinetic, which can be seen from the more considerable value of the determinant coefficient. The kinetic model, The Lagergren Pseudo-second order kinetic, assumes that chemical sorption is the step that determines the reaction rate and predicts behavior throughout the sorption time range. The Lagergren Pseudo-second order kinetic rate of adsorption or desorption depends on the adsorption capacity, not the adsorbate concentration (Huang et al., 2017). It is in line with research (Ikhsan et al., 2018) that the pattern of phosphate binding by SG and ASH adsorbents follows the Langmuir isotherm. The addition of adsorbate concentration will not increase the adsorption rate because the capacity of the active site on the sorbent has been filled with phosphate (Buhani et al., 2009). Based on kinetic modeling with Lagergren Pseudo-second order kinetic, the QE value was 0.22089 M/g for SG sorbent and 0.33333 M/g for ASH sorbent.

Table 3. Desorption parameter data on Lagergren Pseudo-first order kinetic and Lagergren Pseudo-second order kinetic modeling

Desorption Kinetic Parameters	First-order		Second-order	
	SG	ASH	SG	ASH
q_e calculated result (M g^{-1} adsorbent)	0.22113	0.32905	0.22113	0.32905
q_e experiment (M g^{-1} adsorbent)	0.00278	0.00375	0.22089	0.33333
k (g M^{-1} $hours^{-1}$)	0.01382	0.00921	1.29789	0.79086
(R^2)	0.259	0.112	0.998	0.999

QE: The amount of desorbed phosphate at equilibrium time (M g^{-1} adsorbent); k : constant of desorption(g M^{-1} $hours^{-1}$)

Conclusions

The appearance of -NH_2 and -CH_2 groups at wave numbers 1635 cm^{-1} and 1473 cm^{-1} indicates the success of ASH synthesis. The rate of phosphate release by SG and ASH adsorbents followed the Lagergren Pseudo-second Order Kinetic with QE values of 0.22089 M/g for SG sorbents and 0.33333 M/g for ASH sorbents.

Acknowledgment

The authors gratefully thank "Program Studi Kimia FMIPA UNY" that fully funded this research.

References

Audette, Y., O'Halloran, I. P., Evans, L. J., Martin, R. C., & Voroney, R. P. (2016). Kinetics of phosphorus forms applied as inorganic and organic amendments to a calcareous soil II: Effects of plant growth on plant available and uptake phosphorus. *Geoderma*, *279(1)*, 70–76.

Braun, S., McLaren, T. I., Frossard, E., Tuyishime, J. R. M., Börjesson, G., & Gustafsson, J. P. (2022). Phosphorus desorption and isotope exchange kinetics in agricultural soils. *Soil Use and Management*, *38*(1), 515–527.

Buhani., & Suharso. (2010). Modifikasi silika dengan 3-aminopropiltrimetoksisilan melalui proses sol gel untuk adsorpsi ion Cd(II) dari larutan. *Jurnal Sains MIPA*, *16*(3), 177–183.

Buhani., Narsito., Nuryono., & Kunarti, E. S. (2009). Amino and mercapto-silica hybrid for Cd(II) adsorption in aqueous solution. *Indonesian Journal of Chemistry*, *9*(2), 170–176.

Chen, L., Zhao, X., Pan, B., Zhang, W., Hua, M., Lv, L., & Zhang, W. (2015). Preferable removal of phosphate from water using hydrous zirconium oxide-based nanocomposite of high stability. *Journal of Hazardous Materials*, *284*(March), 35–42.

Gypser, S., & Freese, D. (2020). Phosphorus release from vivianite and hydroxyapatite by organic and inorganic compounds. *Pedosphere*, *30*(2), 190–200.

Huang, W., Zhang, Y., & Li, D. (2017). Adsorptive removal of phosphate from water using mesoporous materials: A review. *Journal of Environmental Management*, *193*(May), 470–482.

Ikhsan, J., Sulastri, S., & Priyambodo, E. (2018). Phosphate and nitrate sorption by amine-modified silica as the study of slow release fertilizer. *Journal of Physics: Conference Series*, *1097*(012048), 1-14.

Jalali, M., & Peikam, E. N. (2013). Phosphorus sorption-desorption behaviour of river bed sediments in the Abshineh river, Hamedan, Iran, related to their composition. *Environmental Monitoring and Assessment*, *185*(January), 537–552.

Kondalkar, M., Fegade, U., Attarde, S., & Ingle, S. (2018). Experimental investigation on phosphate adsorption, mechanism and desorption properties of Mn-Zn-Ti oxide trimetal alloy nanocomposite. *Journal of Dispersion Science and Technology*, *39*(11), 1635–1643.

Maslukah, L., Zainuri, M., Wirasatriya, A., & Widiaratih, R. (2020). Studi kinetika adsorpsi dan desorpsi ion fosfat (PO_4^{2-}) di sedimen perairan Semarang dan Jepara. *Jurnal Ilmu dan Teknologi Kelautan Tropis*, *12*(2), 383–394.

Rahmayanti, A., A'Yuni, Q., Hartati., Purkan., & Romanza, I. G. (2020). Synthesis and characterization of silica gel from lapindo mud Sidoarjo. *IOP Conference Series: Earth and Environmental Science*, *456*(012007), 1-7.

Saki, H., Liu, H., & Lennartz, B. (2020). Phosphate sorption onto structured soil. *Soil Systems*, *4*(21), 1–13.

Sdiri, A., Higashi, T., Bouaziz, S., & Benzina, M. (2014). Synthesis and characterization of silica gel from siliceous sands of southern Tunisia. *Arabian Journal of Chemistry*, *7*(4), 486–493.

Sriyanti., Taslimah., Nuryomo., & Narsito. (2005). Sintesis bahan hibrida amino-silika dari abu sekam padi melalui proses sol-gel. *Jurnal Kimia Sains & Aplikasi*, *VIII*(1), 1-8.

Swasdika, F., Trisunaryanti, W., & Falah, L. I. (2021). Hydrotreatment of cellulose-derived bio-oil using copper and/or zinc catalysts supported on mesoporous silica-alumina synthesized from lapindo mud and catfish bone. *Indonesian Journal of Chemistry*, *21*(2), 268–278.

Yang, X., Chen, X., & Yang, X. (2019). Phosphorus release kinetics and solubility capacity of phosphorus fractionation induced by organic acids from a black soil in northeast China. *Canadian Journal of Soil Science*, *99*(January), 92–99.

Zaemi, H., & Tjahjanto, R. T., & Darjito. (2013). Sintesis aerogel silika dari lumpur lapindo dengan penambahan trimetilklorosilan (Tmcs). *Jurnal Ilmu Kimia Universitas Brawijaya*, *1*(2), 208–214.