Modification of natural silica using dimethylamine and the application as a phosphate ion absorption

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Abstract. Natural silica is one of the biggest mining products in Indonesia. Silica has the ability to absorb ions because it has two sites that actively activate silanol and siloxan groups that are accessible. Modifications were made to improve the ability of silica to perform impulses. Water ions if they have very high levels can release marine biota ecosystems, phosphate levels that are too high in waters can cause eutrophication, which is the higher levels of oxygen entering the sea. To reduce phosphate levels, phosphate adsorption is carried out using returned silica. The application of silica as a phosphate ion absorber was analyzed through measurements with a spectrophotometer. Adsorption of phosphate ions using pure silica has a maximum absorption of 0.2533 mg / g and silica after modification can adsorb a maximum phosphate ion of 1,1629 mg / g.

1. Introduction
Natural silica is one of the largest minerals in Indonesia with a total of 0.929 million tons in 2010. Based on Sumatera Barat dalam Angka book in Figures published by BAPPEDA, many minerals produced are limestone, coal, silica stone, clay, and iron ore. Silica is an inorganic oxide which has many uses both for the manufacture of various types of silica-based materials such as ceramics, synthetic zeolites, and organic-inorganic composites as well as directly as in the purification of vegetable oils, pharmaceutical products, detergents, stationary phases in the chromatographic column, and fillers polymer [1].

Silica in the form of natural compounds has a crystalline structure and synthetic compounds in the form of amorphous which can be made from silicate solution or silane reagents, while pure silica is in the form of quartz and cristobalite [2]. Natural silica is composed of several compounds with the main constituent SiO₂ 97.69%, and impurities such as Al₂O₃ 1.182%, P₂O₅ 0.379%, CaO 0.066%, Fe₂O₃ 0.09%. To remove these impurities, the activation is carried out first before modifications are made.

Silica is a chemical compound with the molecular formula SiO₂ (silicon dioxide) which can be obtained from silica minerals, vegetable and crystal synthesis. Silica minerals are compounds that are found in minerals / minerals that contain minerals such as quartz sand, granite, and feldspar that contain silica crystals (SiO₂) [3]. Synthetic silica with tridymite crystal structure can be obtained by heating quartz sand at a temperature of 870 ° C, and silica with a cristobalite structure can be obtained by obtaining
temperatures above 1470 °C [4]. Vegetable silica can be obtained from rice husks and corn cobs through the process of alkalis extraction or ashing.

The primary structure of silica is tetrahedral SiO4, where each one of the silicon atoms is surrounded by four oxygen atoms. SiO4 crystal structure as shown in figure 1.

![Figure 1. Structure of tetrahedral silica.](image)

The silicate skeletal structure is a polymer of tetrahedral SiO4, which forms a three-dimensional polyhedral network through bonds between oxygen in one tetrahedral with another tetrahedral. So as a result of the formation of this silica framework there are pores that are open enough to allow the entry of other molecules by the adsorption process [5].

Activation of natural silica can be carried out physically such as grain size reduction, sifting, and heating with the aim that organic impurities can be removed, enlarge pores, and expand surfaces and chemical activation by acidification and refinement so that inorganic impurities disappear, clean pore surfaces and remove disruptive compounds [6].

Silica can be used as an adsorbent because silica is inert, hydrophilic, has high thermal and mechanical stability, and relatively does not expand in organic solvents. Silica has two active sites namely silanol and siloxane group (Si-OH and Si-O-Si), silanol groups on silica will interact with water molecules, so that the water will deactivate on the surface of silica and the separation process becomes weak because it’s retention power decreases so it needs to be modified to improve the ability to separate silica. The existence of these two active sites allows for modification by changing the cluster on the active side [7].

Silica is relatively unreactive to Cl2, H2, acids and most metals at temperatures of 25°C or higher, but quite reactive to F2, HF solutions, alkali hydroxides, and carbonate fusion [8].

Silica minerals have several chemical properties, including the following:

1. Acid Reaction

Silica is relatively unreactive to acids except hydrofluoric acid and phosphoric acid.

\[
\text{SiO}_2(s) + 4\text{HF}_{(aq)} \rightleftharpoons \text{SiF}_4(aq) + 2\text{H}_2\text{O}_{(l)}
\]

In excess acids the reaction is [9]:

\[
\text{SiO}_2(s) + 6\text{HF}_{(aq)} \rightleftharpoons \text{H}_2(\text{SiF}_6)_{(aq)} + 2\text{H}_2\text{O}_{(l)}
\]

2. Base Reaction

Silica can react with bases especially strong bases such as alkali hydroxides [9].

\[
\text{SiO}_2(s) + 2\text{NaOH}_{(aq)} \rightleftharpoons \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}
\]

Silica have white or other color depending the impurities. Silika as Quartz have white color is the result of weathering rocks that contain major minerals such as quartz and feldspar. Silica is a contain of SiO2, Al2O3, CaO, Fe2O3, TiO2, CaO, MgO, and K2O [10].
Silica need to activation process to remove impurities which are then separated and dried again so that the sand with greater silica content is obtained depending on the quartz conditions of the mining site.

Modification of silica by adding a material to its surface has been widely carried out, such as modification with the addition of Mercaptopropyltrimethoxysilane (MPTS) to obtain the mercapto group, modification with aminopropyltrimethoxysilane (APTS) to obtain an amino group, modification with chloropropyltrimethoxysilane (CPTS) to get the chloro group and which is not an aminopropyltrimethoxysilane (APTS) to obtain an amino group, modification with chloropropyltrimethoxysilane (CPTS) to get the chloro group and non-reagent silane such as -1 amino 2 hydroxy 4 naphthalene disulfonic acid, a glycidoxypropyltrimethoxysilane-linking compound (GPTMS) is used.

The ions in the waters can affect the water quality of these waters. Some of the ions present in waters are sodium, calcium, magnesium, sulfate, phosphate, chloride, and bicarbonate ions. The high level of phosphate ions in water can cause eutrophication which affects water quality. To improve water quality, it is necessary to reduce the use of materials that produce phosphate waste or treat phosphate waste [11].

To reduce and eliminate the content of impurities in the water it is necessary to decontaminate or purify, some commonly used methods are ion exchange with resin, membrane filtration or adsorption method [12].

Phosphate levels in water or wastewater can be determined by the vanadomolibdophosphoric, stannous chloride (SnCl) and ascorbic acid method. Determination by vanadomolibdophosphoric method is the reaction between ammonium molybdate and antimony tartrate potassium with orthophosphate in an acidic atmosphere which forms phosphomolybdic acid compounds and then reduced by ascorbic acid to a blue complex [13].

2. Research Methodology

2.1 Materials and Equipment
The equipment used is: smoothing machine, X-Ray Fluorescence (XRF), UV-Vis spectrophotometer, shaker, Magnetic Stirrer, hot plate, oven, analytical balance, reagent bottles, measuring flasks, erlenmeyers, beaker glass, stirring rods, measuring pipettes, measuring cups, watch glass, spray bottles.

Materials used in this study include: natural silica, 1M HCl, glycidoxypropyltrimethoxysilane (GPTMS), toluene, Dimethylamine (DMA), methanol, ethanol, KH$_2$PO$_4$, filter paper and aquadest.

2.2 Research Procedures

2.2.1 Activation of Silica. Smooth natural silica and sifted using a 45μm shaker. Weighing 25 grams of silica then adding 1 ml of 100 ml HCl and stirring for 24 hours. Neutralize the pH with aquadest and dry it in the oven for about 2 hours at 105°C. Characterize using XRF to determine the composition of the silica constituents.

2.2.2 Making Silica-GPTMS. Weigh 0.1 grams of activated silica and add 0.1 ml of GPTMS and 3.5 ml of toluene anhydrous. Heat at 90°C for 24 hours. Wash the mixture with 0.5 ml of methanol.

2.2.3 Silica Modification. Weigh the silica that has been added by GPTMS as much as 0.1gram, then add 0.5ml of DMA Ethanol (1: 1 v/v). Heat the mixture while stirring at 70°C for 24 hours and rinse with 0.5ml of methanol.

2.2.4 Determination of the optimum pH. Weigh silica by ± 1 gram, adding 25 ml of KH$_2$PO$_4$ into the erlenmeyer that already contains silica. Adjust pH 1, 3, 5, 7, 9 and 11 and stir using a shaker for 2
hours at 150 rpm. Filter until a clear solution is obtained and measure the adsorption using a spectrophotometer.

2.2.5 Determination of optimum contact time. Weigh 1 gram of silica and put it in a 100 ml erlenmeyer. Add 25 ml of KH$_2$PO$_4$ and stir using a shaker until 30 minutes, 60 minutes, 90 minutes and 120 minutes at 150 rpm. Filter with whatman filter paper until a clear solution is obtained. Measuring absorption using a spectrophotometer.

2.2.6 Determination of Adsorption Isotherms Before Modification. Weigh 1 gram of silica before modification as much as 5 pieces and add 25 ml of KH$_2$PO$_4$ 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm each other into a 100 ml erlenmeyer. Stir each mixture using a shaker for 2 hours. Filter the mixture with filter paper and calculate the adsorption of phosphate ions using a spectrophotometer.

2.2.7. Determination of Adsorption Isotherms After Modification. Weigh 1 gram of silica after modifying as many as 5 pieces and add 25 ml of KH$_2$PO$_4$ 5 pm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm into a 100 ml erlenmeyer. Shaker for 2 hours. Filter the mixture with filter paper and calculate the adsorption of phosphate ions using a spectrophotometer.

3. Results and Discussion

3.1 Activation of Silica
Natural silica is blended first using a smoothing machine, then sifted with a 45µm shaker. The silica that will be modified is activated to expand its surface and remove impurities in it. Silica activation is carried out by the addition of HCl, where HCl will bind to impurities such as Fe$_2$O$_3$ and P$_2$O$_5$ with the reaction equation that occurs is:

$$Fe_2O_3(s) + 6 HCl_{(aq)} \rightarrow 2FeCl_3_{(aq)} + 3H_2O_{(l)}$$
$$P_2O_5(s) + 2HCl_{(aq)} \rightarrow 2PCl_5_{(aq)} + 5H_2O_{(l)}$$

After adding HCl, silica is filtered and neutralized again using aquadest. The remaining water molecules are evaporated by heating with an oven at 105°C for 2 hours.

![Figure 2](image.jpg)

Figure 2. Silica before activation (a) and silica after activation(b).

From figure 2 we can see the difference in silica before modification and after verification. Silica before being activated has a brownish color and after activation using HCl 1M silica is whiter and cleaner.

3.2 Modification
 Modifications were made to improve the properties and increase the benefits of silica. In this study, silica was modified with dimethylamine, for modification with amine compounds used a connecting
compound containing a silane group namely glycidoxypropyltrimethoxysilane (GPTMS). The connecting compound is used because some chelating groups with ions do not contain reactive functional groups for the silanization process.

In previous studies, silicate monomers were made with a methacrylate crosslinker with dimethylamine and diethylamine modifiers and characterization of the capillary column was made.

GPTMS added silica and toluene anhydrous then heated at 90°C for 24 hours so that the silane group binding process to silica is maximal.

Silica which has been binding GPTMS then modified using dimethylamine which has been dissolved with ethanol (1:1). The mixture is heated at 70°C for 24 hours to maximize the binding of dimethylamine to GPTMS. GPTMS reaction with silica: [14]

![Figure 3. Reaction between silica and GPTMS.](image)

In the modification process, it is estimated that the reaction between dimethylamine and C = O (ester) group of the connecting compound produces an amide compound with a tertiary amide as an anion exchange group and the reaction between dimethylamine and the COC group (epoxy) of the connecting compound produces an amine compound with a tertiary amine as the amine group anion exchange [15].

### 3.3 Adsorption

3.3.1 Determination of the optimum pH

| Number | pH | Concentration before contact (ppm) | Concentration after contact (ppm) | adsorbed concentration (ppm) | adsorbed concentration (mg/g) |
|--------|----|-----------------------------------|----------------------------------|-----------------------------|-----------------------------|
| 1      | 1  | 3,613138686                      | 0,328467153                     | 3,284671533                 | 0,082116788                 |
| 2      | 3  | 3,97810219                       | 0,474452555                     | 3,503649635                 | 0,087591241                 |
| 3      | 5  | 8,649635036                      | 3,613138686                     | 5,03649635                 | 0,125912409                 |
| 4      | 7  | 11,71532847                      | 5,729927007                     | 5,98540146                 | 0,149635036                 |
| 5      | 9  | 12,08029197                      | 6,240875912                     | 5,839416058                 | 0,145985401                 |
| 6      | 11 | 13,97810219                      | 10,62043796                     | 3,357664234                 | 0,083941606                 |
Determination of optimum pH is carried out under conditions of mass adsorbent, contact time and constant concentration. pH was varied at pH 1, 3, 5, 7, 9, and 11. The volume and mass of the adsorbent were constant, in 25 ml and 1 gram. The optimum pH is determined by the adsorption of phosphate ion solution (PO$_4^{3-}$).

The pH value can affect the adsorption process, affects the charge distribution on the surface due to the protonation reaction, or deprotonation of the adsorbent active site, pH can also affect the adsorbate species in solution. The optimum pH is determined through the adsorption process of the phosphate ion solution [16,17].

From the test data it was found that the maximum absorption capacity of silica occurs at pH 7 of 0.149635036 mg/g.

3.3.2 Determination of optimum contact time

| No | Contact time (minute) | adsorbed concentration (ppm) | adsorbed concentration (mg/g) |
|----|-----------------------|-------------------------------|-------------------------------|
| 1  | 30                    | 9,031007752                  | 0,225775194                  |
| 2  | 60                    | 12,44186047                  | 0,311046512                  |
| 3  | 90                    | 13,68217054                  | 0,342054264                  |
| 4  | 120                   | 15,3875969                   | 0,384689922                  |

From the test data it was found that the maximum absorption capacity of silica occurs at pH 7 of 0.149635036 mg/g.
Determined at the constant pH and concentration. The contact time on the adsorption of the solution varied in 30, 60, 90, and 120 minutes. The volume and mass of the adsorbent remains 25 ml and 1 gram. The optimum contact time is carried out by adsorption of the phosphate ion solution.

Based on the research results silica adsorbs the maximum phosphate at the contact time for 2 hours, amounting to 0.384689922 mg / g.

3.4 Adsorption isotherms
The adsorption isotherm is used to determine the adsorption process that occurs at equilibrium. The adsorption isotherm is obtained by channeling the variables in the graph that will produce a linear line equation that will be used to estimate the adsorption mechanism that occurs. In this research, Langmuir adsorption isotherm is used [18,19].

In Langmuir isotherms it is assumed that silica surface has a number of adsorption sites that are proportional to the surface area of the adsorbent. Each active site of adsorbent can only adsorb one adsorbate molecule to form a monomolecular adsorption layer. If the active adsorption site is not saturated with the adsorbate molecule, then the increase in adsorbate concentration is always accompanied by an increased number of adsorbed ions [20,21]. However, if the active site of the adsorbent has been saturated, then the increase in the concentration of the adsorbate relatively does not increase the number of adsorbed ions.

3.4.1 The phosphate ion (PO$_4^{3-}$) adsorption isotherm to silica before modification

| No | C (ppm) | Ce(mg/L) | Qe(mg/g) | Ce/Qe |
|----|---------|----------|----------|-------|
| 1  | 5       | 0.8139   | 0.087    | 9.3326453 |
| 2  | 10      | 5.3875   | 0.122    | 44.127283 |
| 3  | 15      | 9.4961   | 0.153    | 62.025474 |
| 4  | 20      | 13.5271  | 0.180    | 75.054652 |
| 5  | 25      | 16.7829  | 0.182    | 92.127683 |

![Isoterm Langmuir Curve](image)

Figure 6.Curve of Isoterm adsorption silica before modification

The Langmuir adsorption isotherm graph is obtained by passing Ce / Qe (g / L) to Ce (mg / L). From the resulting graph figure 6, the y line equation is obtained = 3.9472x - 2.6744 with a correlation coefficient of $R^2 = 0.9776$. From the equation, the Langmuir qmax and KL adsorption isotherm parameters are obtained. Qmax value is calculated from the slope line that is equal to 0.2533 mg / g. The KL value was calculated from the line equation intercept of 0.0947 L / mg. Langmuir constant
(KL) is the constant equilibrium from the process adsorption. The greater the KL value, the greater the adsorption rate [23].

### 3.4.2 Isotherm adsorption of phosphate ions ($PO_4^{3-}$) to silica after modification of dimethylamine

#### Table 4. Adsorption isotherm of silica after modification

| No | C  | Ce(ppm) | Qe(mg/g) | Ce/Qe |
|----|----|---------|---------|-------|
| 1  | 5.0775 | 1.5116 | 0.0891 | 16,96520763 |
| 2  | 10.8914 | 3.6046 | 0.182 | 19,79461834 |
| 3  | 16.7054 | 6.5503 | 0.254 | 25,80890465 |
| 4  | 21.5891 | 9.341 | 0.306 | 30,50620509 |
| 5  | 25.155 | 9.6511 | 0.288 | 33,56904348 |

**Figure 7. Curve of Isoterm adsorption silica before modification.**

The Langmuir adsorption isotherm graph is obtained by passing $Ce / Qe \ (g / L)$ to $Ce \ (mg / L)$ [24,25]. The obtained line equation is $y = 0.8599x + 11.67$ with a correlation coefficient of $R^2 = 0.9867$. Langmuir equation:

$$\frac{Ce}{Qe} = \frac{1}{qmKL} \left( \frac{1}{qm} \right) Ce$$  \hspace{1cm} (1)

From the equation, the Langmuir qmax and KL adsorption isotherm parameters are obtained. Qmax value is calculated from the slope line that is equal to 1.1629 mg / g. The KL value was calculated from the line equation intercept of 0.099 L / mg.

#### Table 5. Parameters of phosphate ion adsorption isotherms in silica before and after modification

| No | Sample                      | The Langmuir adsorption isotherm |
|----|------------------------------|----------------------------------|
| 1  | Silica before modification  | $R^2 : 0.9776$  
$q_{maks} : 0.2533 \ mg/g$  
$K_L : 0.0947 \ L/mg$ |
| 2  | Silica after modification   | $R^2 : 0.9867$  
$q_{maks} : 1.1629 \ mg/g$  
$K_L : 0.099 \ L/mg$ |
Table 5 shows that silica before modification and after modification follows the Langmuir isotherm pattern. Adsorption capacity was 0.2533 mg / g and 1.1629 mg / g, respectively.

4. Conclusion
Silica is activated using 1M HCl to increase SiO$_2$ content by removing impurities. Modification of silica with dimethylamine (DMA) used glycidoxypropyltrimethoxysilane (GPTMS) linking compounds. pH 7 and contact time 120 minutes is the optimum condition of adsorption. The adsorption isotherm study shows the adsorption of phosphate ions (PO$_4$$^{3-}$) with pure silica and dimethylamine modified silica meets the Langmuir isotherm equation. Maximum capacity (qmax) from adsorption process used silica before modification is 0.2533 mg / g and after modification 1.1629 mg/g while the Langmuir constant values are 0.0947 L/mg and 0.099 L/mg.

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