Modified Natural Silica Dimethylamine for Optimization of Sulfate Ion Absorption Using the Batch Method

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Abstract. Sulfates are compounds that are often used in various industrial activities. Sulfate wastes with high concentrations can cause an imbalance in the natural sulfur cycle which causes the leaching of toxic sulfides which leads to environmental damage. Adsorption is an effective way of dealing with waste. Silica is an adsorbent that is often used for the adsorption process. on DMA-modified silica. Characterized by using infrared spectra, microscope scanner and adsorption of sulfate solutions with various concentrations and contact times. The results showed that the use of modified DMA silica had better absorption than activated silica seen from the frendulich isotherm pattern with a regression coefficient $R^2 = 1$. Absorption capacity at 60 minutes was 0.82754 mg / g.$^{-1}$.

1. Introduction
Sulfates are a common component found in many waters and wastewater. The main source of sulfate in wastewater is the use of sulfuric acid in many chemical analysis activities. Sulfate is an inert compound, non-volatile and non-toxic, however, if the sulfate concentration is high it can cause an imbalance in the natural sulfur cycle which causes the release of toxic sulfides which can cause environmental damage [1].

Various techniques have been used to remove these sulfate ions or anions including chemical deposition, solvent extraction, ion exchange, adsorption, membrane separation and electrochemical techniques. The adsorption process has advantages including a more flexible, simpler, easier and more effective form of removing ions or anions, especially at low concentrations [2].

In the adsorption process, silica can be used as an adsorbent [3]. Silica is able to bind inorganic compounds but silica has two active sides in the form of silanol (Si-OH) and siloxan (Si-O-Si) groups which reduce its absorption effectiveness [4]. To interact more strongly between the two compounds, silane can be used which functions as a cross-link which is a connecting compound. In 2020 Budhi et al succeeded in conducting research on making monolith columns by making polymers in silica capillaries using glycydyl methacrylate (GMA) as a monomer, azobisisobutyronitrile (AIBN) as an initiator, ethylene dimethacrylate (EDMA) as a crosslinker and a porogen 1,4 butanadiol, 1 - propanol, and water after the formation of the polymer is further modified using Dimethylamin (DMA) as a modifier [5]. Modifications with monolithic columns can be used as separation media in ion chromatography. Ion chromatography is an analytical technique that can be used to determine cations or anions in shared samples at lower concentrations [6]. In the study GPTMS is used as a connecting
compound that forms epoxy networks. Then silica is used with amine compounds [7] which in this study used Dimethylamine. DMA modified silica is used as an absorber for sulfate anions for the determination of anions using ion exchange chromatographic analysis techniques. The purpose of this study was to test the feasibility of DMA modified silica as an absorbent for sulfate anions.

2. Experimental

2.1. Apparatus and Chemicals
The materials used are natural silica, GPTMS, Dimethylamine, Ethanol, Methanol, Na2SO4, C7H5NaO2 and distilled water. The tools used in this study were glassware, analytical balance (ABS 220-4), shaker (model: VRN-480), pH meter (HI2211), magnetic stirrer (MR Hei Standard), filter (BS410), spray bottle, oven, mortar and alung, and HIC (Prominence LC-20 AD SP).

2.2. Preparation of standard sulfate solutions and the mobile phase of sodium benzoate
Standard anion solutions with a concentration of 1000 ppm were prepared by dissolving 0.148 grams of Na2SO4 in a 100 ml volumetric flask, adding distilled water to the limit. Then until homogeneous and store in a reagent bottle. The working solution is carried out by diluting the standard solution. Then the mobile phase of sodium benzoate was started by dissolving 7.205 g of sodium benzoate in a 50 ml volumetric flask, then adding distilled water to the limit mark, then stirring until it was homogeneous. The 4mM sodium benzoate solution was prepared by diluting the main solution of natrium benzoate.

2.3. Silica Preparation and Modification of silika-GPTMS with DMA
Natural silica that has been refined with a grinding machine at PT. Semen Padang was then sieved with a mesh sieve at the SMK-SMAK Padang Laboratory to obtain a particle size of 45 µm, then 35 grams of 45 µm of silica were immersed and stirred in 350 ml of 1M HCl for 24 hours. PH neutralization with distilled water and then dried in an oven at 105 °C for 2 hours. 25 grams of activated silica were then added 25 ml of GPTMS and 87.5 ml of toluene, then stirred for 24 hours at 90 °C, then the mixture was washed with 12.5 ml of methanol. 23 grams of silica-GPTMS was modified by adding 11.5 ml of DMA then 11.5 ml of ethanol (1: 1 v / v). The modified silica was then heated at 80 °C for 4 hours then oven and rinsed with methanol.

![Figure 1. Formation of Silica-GPTMS](image-url)
2.4. Research treatment with the batch system
The effect of contact time is carried out with take 10 ml of sulfate solution put into each Erlenmeyer then contact with 0.5 grams of silica with a variation of contact time of 10 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes and 60 minutes then shaken at 150 rpm, then filtered using filter paper, the filtrate obtained is then measured for its concentration with HIC. Then The effect of solution concentration is carried out by taking 10 ml of sulfate solution with various concentrations of 25 ppm, 50 ppm, 75 ppm, 100 ppm, 125 ppm and 150 ppm were put into each Erlenmeyer then contacted with ± 0.5 gram silica using a shaker for 60 minutes at 150 rpm, then filtered by using filter paper obtained the filtrate which is then measured the concentration using HIC.

2.5. Absorption capacity comparison
± 0.5 gram of active silica and DMA-modified silica each were added to each Erlenmeyer and then added with 10 ml of sulfate solution with a concentration of 50 ppm. Shaker with a speed of 150 rpm, then filtered using filter paper, the filtrate obtained is then measured for its concentration with HIC.

3. Results and Discussion

3.1. The effect of contact time on the absorption of sulfate anions using DMA modified natural silica as adsorbent
The variation of contact time aims to determine how long it takes DMA-modified silica to absorb sulfate anions. Variations in determining contact time were 10, 20, 30, 40, 50 and 60 minutes at a concentration of 50 ppm. The results of the duration of contact with DMA-modified silica can be seen in the following figure 2.

![Figure 2](image.png)

Figure 2. Effect of contact time on absorption of sulfate anions using DMA-modified silica as adsorbent (under 10 ml of sulfate solution, 0.5 g of silica, stirring speed of 150 rpm for 10 to 60 minutes).

The absorption capacity of sulfate anions increases because the longer the contact time is carried out, the greater the contact time between the adsorbent and the adsorbate [8]. So that the sulfate anion binds more to the adsorbent. This is because the number of active sites increases with the longer the contact time, the more sulfate anions are bound to the active side.
3.2. Effect of concentration on the absorption of sulfate anions, using DMA modified Natural Silica as adsorbent.

The concentration variations used in this study were 25 ppm, 50 ppm, 75 ppm, 100 ppm, 125 ppm, and 150 ppm. The results can be seen from Figure 3.

![Figure 3](image)

**Figure 3.** Effect of concentration on absorption of sulfate anions using DMA-modified silica as adsorbent (in 10 ml of sulfate solution, 0.5 g of silica, stirring speed 150 rpm for 60 minutes).

The results that can be seen from the figure are an increase in the absorption capacity of sulfate anions at a concentration of 25 ppm to 150 ppm. This happens because the greater the concentration of a solution, the more molecules collide and bind to the adsorbent, thereby increasing its adsorption ability. This is related to the number of active sites present in the adsorbent, when the number of active sites is greater, the absorption that occurs will also be greater, when the concentration is greater the number of ions absorbed will be the same as the available active sites.

The absorption capacity of an adsorbent is influenced by several factors that affect the absorption capacity of an adsorbent and usually has a specific adsorption isotherm pattern. Some of the factors that affect the absorption process are the type of adsorbent used, the type of material absorbed, the surface area of the adsorbent, the temperature and the concentration of the absorbed material. Due to these factors, each adsorbent that absorbs one substance with another will not have the same adsorption isotherm pattern. In the adsorption process in solution there are two types of adsorption isotherms that are often used, namely the Langmuir and Freundlich adsorption equations.

The measurement capacity of the resulting variation in filtrate concentration after adsorption is then entered into the standard straight line equation so that the line equation $y = 1114x + 2566$ is obtained with a linear regression coefficient $r = 0.993$ and can be expressed in langmuir and freundlich isotherms. isotherm in the following figure 4.
Figure 4. Isoterm Langmuir

Figure 5. Freundlich's isotherm.

The absorption capacity of the sulfate solution has a value of \( R^2 = 0.161 \) for the Langmuir isotherm and \( R^2 = 1 \) for the Freundlich isotherm can be seen from the figure above. Correlation coefficient data (\( R^2 \)) can be used to determine which isotherm pattern is suitable for the test data of this study. If the \( R^2 \) value is getting closer to number 1, it can be concluded that there is a greater influence and there is a stronger variable bond \([11]\).

From the two graphs above, the isotherm pattern tends to follow the Freundlich isotherm equation more than the Langmuir isotherm because it has an \( R^2 \) value for the Freundlich curve of 1. Then the adsorption capacity of dimethylamine silica modified to sulfate is calculated using the Freundlich isotherm equation. In the Freundlich isotherm pattern, the absorption occurs physically so that the adsorbent surface is absorbed more \([12]\).
3.3. Comparison of the adsorption capacity of Silica and Silica-GPTMS-DMA as adsorbent

The comparison of the adsorption capacity of silica and silica-GPTMS-DMA can be seen in the following figure 6.

Figure 6. Comparison of the absorption capacity of silica and silica-GPTMS-DMA at a concentration of 50 ppm, silica-GPTMS-DMA 0.5 g, contact time of 60 minutes at a speed of 150 rpm.

The absorption capacity of sulfate anions with activated silica as adsorbent has the ability to bind less sulfate anions, namely 0.76362 compared to DMA-modified silica, which is 0.82745, this is due to the more active sites contained in the modified thermethylamine silica so that it can increase the absorption capacity. anion. sulfate.

4. Conclusion

Based on the research that has been done, that modified silica can be used as an adsorbent for the absorption of sulfate anions which can be seen based on the adsorption capacity at the contact time variation of DMA modified silica as an absorbent sulfate anion greater than activated silica. Determination of the most suitable DMA modified silica adsorption capacity is to use the Freundlich isotherm equation compared to the Langmuir isotherm equation.

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