Activation and Modification of Natural Silica for Anion Adsorbent

by Rahadian Zainul Et.al

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Abstract. Silica is a mineral that is abundant in the earth's surface. Silica has also been used in human civilization, such as making glass, electronic devices, adsorbents, fertilizers and others. Utilization of natural silica requires technology that is reliable enough so that impurities in the natural silica do not interfere with its use. In this study, tests have been carried out on natural silica, such as chemical and physical activation, reactions with certain reagents and also modifications made to the natural silica. The desired result is that natural silica can be used as an adsorben, ion exchange and also a stationary phase in the chromatography column. From this research a natural silica modification has been obtained using dimethylamine (DMA) to convert natural silica into positive charge so that it can be used to increase the absorption of some anions.

1. Introduction

Silica is a compound resulting from the polymerization of silicic acid, which is composed of tetrahedral SiO_4 unit chains with the general formula SiO_2. Silica is the second largest constituent of the lithosphere (27.61%) after oxygen (46.46%). As much as 60% of basalt and granite rocks are composed of SiO_2 and five of the seven primary mineral groups (except phosphate and carbonate groups) contain Si. Crystalline silicate minerals (SiO_2) include quartz, tridymite and cristobalite, while non-crystalline ones are opaline silica which is formed biologically from the silification process of grass. [1]

Silica as a compound found in nature has a crystalline structure, while as a synthetic compound it is amorphous. Silica is an excellent insulator that reaches temperatures up to 1000°C. Silica is formed through strong covalent bonds, and has a clear local structure, where four oxygen atoms are bonded in a tetrahedral angle position around the central atom, namely the silicon atom. In nature, silica is found in the form of cristobalite, tridymite, quarts, and amorphous. [2]

In the preliminary test, analysis of the chemical composition of natural silica using XRF was carried out and the percentage of SiO_2 was 97.993% and several impurity compounds including Al_2O_3 0.951%, P_2O_5 0.261%, CaO 0.079%, Fe_2O_3 0.482%. The results of this test indicate that silica from nature still contains a lot of impurities. To improve the character of natural silica so that it can be used as a chromatographic stationary phase, it is necessary to first activate it.

Activation of natural silica can be carried out physically or chemically. Physical activation is carried out by reducing grain size, sieving and heating, the goal is to remove organic impurities, enlarge pores and increase the surface area. Meanwhile, chemical activation can be carried out through acidification and alkalization which aims to remove inorganic impurities, clean pore surfaces and remove disturbing compounds.

To increase the absorption or adsorption of silica, an activation process is carried out. Activation is a physical change in which the surface area of the silica becomes larger because the impurities that clog the pores are freed. There are 2 ways to carry out the activation process, namely physics and chemistry. The physical activation process is carried out by reducing grain size, sieving and heating which aims to remove organic impurities and evaporate water trapped in the sample crystal pores so that the number of pores and specific surface area increases.

Chemical activation is carried out by immersing raw materials in chemicals such as H_3PO_4, $ZnCl_2$, KOH, HCl, H_2SO_4, $CaCl_2$, K_2S, NaCl, and others [3,4]. The advantages of chemical activation, among others, require a low temperature, result in higher purity and controllable micropores. Activation with acid can be carried out using a solution of HCl, H_2SO_4 and H_3PO_4 which aims to clean the pore surface and remove disturbing compounds. Activation using mineral acids will dissolve the components of Fe_2O_3, Al_2O_3, CaO and MgO which fill the adsorbent pores. This will result in the opening of closed pores thereby increasing the surface area of the adsorbent. [5,6]

Silica is polar so it can be used for the analysis of polarity based compounds. Activated and modified natural silica with certain reagents can become charged so that it can be used as an adsorbent for ions. In this study, dimethylamine (DMA) was used as a modifying compound and glycidoxypropyltrimethoxysilane (GPTMS) as a connecting compound. The modified silica was then tested for its absorption capacity for anions. [7,8].

2. Experimental

2.1. Apparatus

Determination of the elemental content in natural silica using XRF-PANAlytical Epsilon, determination of crystal form and compounds in natural silica using XRD (X'Pert Powder PANAlytical Pw 90/60), determining silica morphology using SEM (Phenom TM type: Pro X), determination of wave number using FTIR (Perkinelmer type: FTIR Spectrometer Frontier), wavelength determination using Genesys 20, as well as other tools such as Stirer (Multimatic-5N), Shakker, glassware, sieve, oven, analytical balance, reagent bottles, flasks measuring, erlenmeyer, spray bottle, stirring rod, dropper pipette.

2.2. Chemicals

All of chemicals are obtained from Merck, unless otherwise noted. glycidoxypropyltrimethoxysilane (GPTMS), dimethylamine (DMA), HCl, distiled water (H_2O), toluen (C_7H_8), ethanol (C_2H_5OH), methanol (CH_3OH), $K_2Cr_2O_7$, KH_2PO_4, $NaNO_3$, $NaNO_2$ and natural silica from Brataco.

2.3. Research procedure

2.3.1. Sample preparation. Natural silica is ground and sieved to obtain a particle size of about 45 µm.

2.3.2. Activation of natural silica with HCl. The natural silica sample was weighed as much as 25 g and put in each of the 4 beaker 600 ml, added to each beaker 250 ml HCl with a concentration of 0.01 M, 0.1 M, 1 M and 2 M. Silica samples immersed in HCl were stirred for 24 hours. Neutralized the pH with distilled water and dried in an oven for about 2 hours at 105°C. Activated silica was tested with XRD and XRF to determine changes in structure and composition.

2.3.3. Modification of natural silica with DMA using GPTMS as the connecting compound. First, 25 g of activated natural silica was reacted with 25 ml of GPTMS and 87.5 ml of toluene. The mixture was

stirred at 90°C for 24 hours to form silica-GPTMS and then washed with 12.5 ml of methanol. 23 g of silica-GPTMS was modified with 11.5 ml of DMA dissolved in 11.5 ml of ethanol (1:1 v/v) to form silica-GPTMS-DMA. The DMA-modified silica was then heated for 4 hours at 80°C, after which it was rinsed with methanol.

2.3.4. DMA-modified silica absorption test on anions commonly found in nature. Absorption is carried out by a batch system. Weigh 1 g of DMA-modified silica put in a 250 ml beaker, add 25 ml of each of the following anions NO_3^-, NO_2^-, CrO_4^{2-} and PO_4^{3-} at variations in pH and variations in contact time in order to obtain optimum conditions. Next, vary the concentration of each anion to determine the absorption capacity and compare it with the absorption capacity before the silica is modified. Determine the amount of anion concentration that is absorbed in each treatment to determine the optimum conditions

3. Results and Discussion

The natural silica used is natural silica obtained from Indonesia. Natural silica consists of many other compounds which act as impurities on the natural silica. So that in order to get cleaner natural silica, several actions is needed to get the silica with the desired conditions. Furthermore, the silica is modified using DMA so that the modified silica is positively charged and can be used as an anion absorber through the reaction of positive ions with negative ions. The results obtained can be described in the following section.

3.1. Activation of natural silica with HCl

Natural silica is activated using HCl. The data from XRF shows the content of compounds contained in activated natural silica at various concentrations. A comparison of the concentration of silica content with impurity content is made as in Table 1.

Table 1. Comparison of activated silica content at various concentrations of HCl.

Compound Concentration (%)	Silica before activation	0.01 M HCl activated silica	0.1 M HCl activated silica	1 M HCl activated silica	2 M HCl activated silica
Al_2O_3	0,951	0,637	0,627	0,61	0,616
SiO_2	97,993	98,808	98,893	98,893	98,924
P_2O_5	0,261	0,246	0,26	0,309	0,27
K_2O	0,081	0,027	0,026	0,021	0,025
CaO	0,079	0,052	0,051	0,054	0,05
TiO_2	0,024	0,014	0,015	0,015	0,013
V_2O_5	0,001	0,001	0,001	0	0,001
Cr_2O_3	0,069	0,032	0,03	0,02	0,024
MnO	0,002	0,001	0,001	0,001	0,001
Fe_2O_3	0,482	0,137	0,052	0,032	0,036
ZrO_2	0,003	0,003	0,003	0,004	0,003
Ag_2O	0,049	0,039	0,039	0,038	0,035
In_2O_3	0	0	0	0,004	0,001
WO_3	0,003	0,001	0,001	-	0,001
Cl	0,002	0,002	0,002	0,001	0

From Table 1 it can be seen that, the SiO_2 content in each treatment increased from 97.993% to 98.808%, 98.893%, 98.893% and 98.924% for activation using 0.01 M, 0.1 M, 1 M and 2 M HCl

respectively. participate. Meanwhile, the smallest concentration of Al_2O_3 was found in activated silica with 1 M HCl, namely 0.61%. These results indicate that activation with HCl was able to increase SiO2 levels and reduce impurity levels.

According to Kartika [9], the crystallinity of natural silica can be identified by the number of peaks that appear in the XRD spectra, the fewer peaks that appear in the spectra, the better the crystallinity of natural silica. Based on the XRD test, it was found that 0.01 M HCl activated silica had 23 peaks, 0.1 M HCl activated silica had 20 peaks, 1 M HCl activated silica had 18 peaks and 2 M HCl activated silica had 24 peaks.

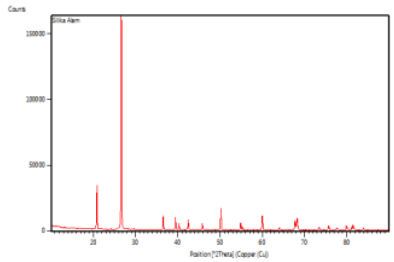

Figure 1. The XRD spectra of natural silica.

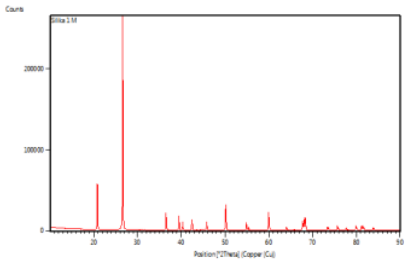

Figure 2. The XRD spectra of natural silica were activated by 1 M HCl.

Figure 1 and Figure 2 show that the highest peak is at position 2Θ = 26.6819° which is the peak of SiO_2 crystals in natural silica and activated natural silica. This data was obtained from the International Center for Diffraction Data-Inorganic Crystal Structure Database (ICDD-ICSD). By using the Scherrer equation, the crystal size of natural silica was 144.42 nm and the average grain size was 77378.10^{-7} m.

By using the Scherrer Equation for natural silica activated by HCl, it can also be calculated the crystal size and average grain size of natural silica where the smaller the grain size, the better the crystallinity. For crystal size and grain size of natural silica using HCl 0.01 M; 0.1 M; 1 M and 2 M are 203.03 nm, 130115.10^{-6} m ; 177.66 nm , 152351.10^{-6} m; 157.92 nm, 132836.10^{-6} m; 177.66 nm, 148812.10^{-6} m respectively. It can be seen that the best crystal size is in the 1 M HCl and the best grain size of acid activated silica is 0.01 M HCl activated silica.

Figure 3 shows the morphology of natural silica at a magnification of 250 times. In the figure, it can be seen that the silica surface morphology tends to be flat, with random, irregular grains and varying sizes. Some of the impurity powders stick to the surface of the granules and there are no visible pores where absorption occurs. It can be concluded that the pores found in natural silica are very small (micropores). From the figure it can also be seen that the size of some grains is about 5-10 µm. If linked to the results of measurements using XRD (average grain size of natural silica: 77378.10^{-7} m = 7.73 µm), it can be concluded that the SEM and XRD data support each other.

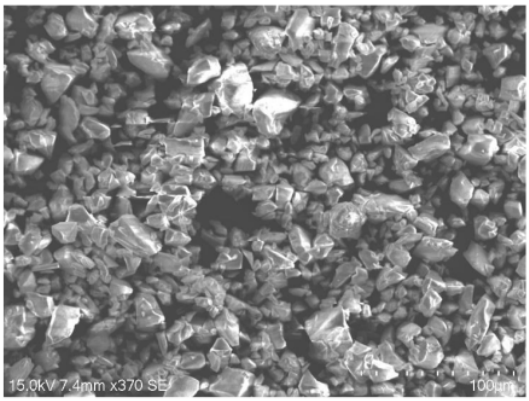

Figure 3. Natural silica morphology with magnification of 250 times.

3.2. Modification of natural silica with DMA using GPTMS as the connecting compound

The activated natural silica is further modified using DMA. The addition of DMA directly cannot be done because silica is not reactive. This requires a connecting compound, namely GPTMS. GPTMS together with toluene are added to natural silica to form the silica-GPTMS layer. The newly formed silica-GPTMS is reacted with DMA to form silica-GPTMS-DMA. Each stage of the change in the form of silica above is tested using FTIR. The results can be seen in Figure 4.a, 4.b, and 4.c.

In Figure 4.a shows the asymmetric strain of Si-O at wave number 1050.69 cm^{-1} and the symmetrical strain of Si-O at wave number 696.24 cm^{-1}, then in Figure 4.b shows the C-C strain at wave number 2110.24 cm^{-1} shows the presence of GPTMS in natural silica and Figure 4.c shows the peak of the amide group (C = O) at wave numbers 1800-2100 cm^{-1} which confirms that DMA has also bound to the silica. In the modification process it is estimated that there will be a reaction between dimethylamine and the C = O (ester) group of the linking compound to produce an amide compound with a tertiary amide as an anion exchange group and the reaction between dimethylamine and the C-O-C (epoxy) group of the linking compound to produce an amine compound with a tertiary amine as the ion exchange group.

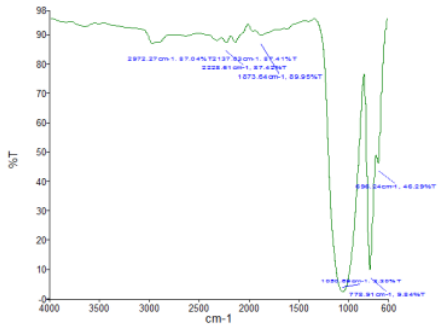

Figure 4.a. Natural Silica Spectrum.

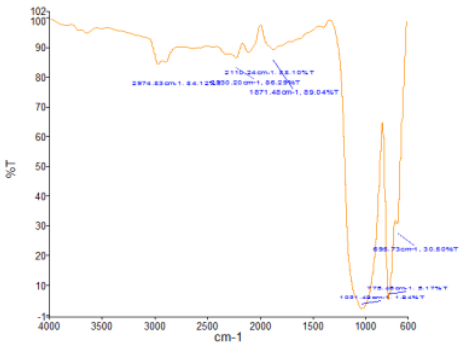

Figure 4.b. Silica-GPTMS spectrum.

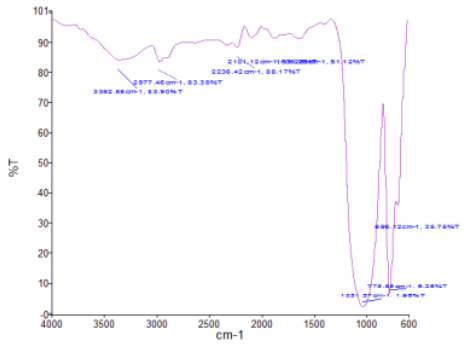

Figure 4.c. Silica-GPTMS-DMA spectrum.

3.3. DMA-modified silica absorption test on anions commonly found in nature

Natural silica that has been modified with DMA is tested to see whether the silica can absorb more anions than before being modified. For this, several anions were tested, such as nitrate, nitrite, phosphate and chromate. The results showed that the amount of anions absorbed was greater in the modified natural silica than the unmodified natural silica.

In Table 2 it can be seen that there is a variation between pH, contact time and the increase in absorption for each anion. The highest increase occurred in nitrate anions which reached 2100% and the lowest was in chromate anions, namely 57.54%. However, overall it can be said that the natural silica which has been modified with DMA can increase the anion absorption.

Table 2. The absorption conditions of some anions use natural silica before and after modification.

Anion	pH	Contact time	Absorption capacity (mg/g)		increased absorption
			before modifcation	after modification	
PO_4^{3-}	7	120 minute	0.2533	1.1629	359,1 %
NO_2^-	6	60 minute	0.1660	1.0182	513,4 %
NO_3^-	8	90 minute	0.0490	1.0781	2100 %
CrO_4^{2-}	2	90 minute	0.6500	1.0240	57,54 %

4. Conclusion

The conclusion of this study is that natural silica can be activated using 1 M HCl to obtain natural silica which is cleaner than impurities, DMA modified silica can be used as an adsorbent to absorb anions at optimum pH and contact time conditions, the maximum absorption capacity obtained is higher rather than the absorption capacity of natural silica before modification and the resulting natural silica has a non-uniform morphology so that it cannot be used as a stationary phase in ion chromatography, it is necessary to re-form silica from natural silica by controlling the size and shape of the silica.

Acknowledgment

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