Eco-Friendly Methods of Silica Extraction from Pyrophyllite Rocks Using Sol-Gel versus Alkali Fusion Method

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Abstract. Silica is the most abundant compound on the Earth's surface. The content of silica can be found in agricultural waste ash and mineral rocks. Extracting silica from natural sources is advantageous due to its economic feasibility and easily obtained. Silica has a wide range of applications, such as in fertilizers, adsorbents, organic reaction catalysis, biofuels/alternative energy production, and as an antimicrobial agent. One type of rock that contains the highest amount of silica is Pyrophyllite. Recent research trends have focused on various methods and sources for silica extraction, yet extracting silica from mineral rocks presents its own challenges. Pyrophyllite rock contains a high amount of silica, but its extraction is quite difficult due to the presence of crystalline silicate mineral phases. This study aims to compare the silica extraction process on Pyrophyllite rocks from Malang using the sol-gel method versus the alkali fusion method.

1 Introduction

Silica is the most abundant compound on the earth's surface with levels of 50-70%, as a component of soil. Silica deposits are found in many mineral rocks and several types of plants [1]. Many types of minerals with high silica content such as kaolin, bentonite, albite, muscovite, montmorillonite, mullite, illite, and pyrophyllite. Pyrophyllite is a unique alumino-silicate mineral with a silica tetrahedral structure layered with hydroxylated alumina (1:2). The layered structure of pyrophyllite allows the inter-layer space to be filled with cations and water molecules which can be dehydrated under thermal conditions. Pyrophyllite is often used extensively in manufacturing refractories, ceramics, insulators, rubber fillers, paper, paints, and porous materials [2]. Pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) has a high silica content between 60-82% [3]. The high silica content in Pyrophyllite can provide potential as a source of silica (SiO_2) for the manufacture of advanced materials.

Some research trends, silica (SiO_2) can be extracted from various sources such as agro-waste ash, urban solid waste, sand, and mineral rocks. Silica has a wide range of roles such as adsorbents, composites, organic reaction catalysts, biofuels or clean energy production, and antimicrobial agents. Previous research has extracted silica from agricultural waste such as rice husk ash [4], palm bunch ash [5], and sugarcane bagasse ash [5] with a silica yield obtained of 80-98%.

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On the other hand, extraction of silica from rocks such as kaolinite [5], quartzite [6], and bentonite [7] obtained a silica yield of about 35-94%. The methods commonly used in silica extraction are the sol-gel and alkali fusion methods. Both of these methods can be affected by the silica phase and impurities in the sample. The approach to change the structure or phase of the sample can be carried out by thermal treatment through calcination to increase the amount of amorphous silica that can be extracted from the sample, while impurities can be reduced through pre-treatment of leaching. Impurities in rocks are metal oxides such as Al_2O_3, CaO, Fe_2O_3, TiO_2, and V_2O_5 [8]–[11]. Whereas in the ashes of agricultural waste are in the form of metal oxides which dissolve easily in slight acids such as K_2O, and Na_2O and some oxides of sulfur and phosphorus [12]–[15].

In the extraction of silica from the ashes of agricultural waste is relatively easier than from rock. Silica in plants tends to be amorphous while silica in rocks tends to be predominantly crystalline. In addition to the phase difference, the presence of metal oxide impurities can also affect the extraction process. When considering eco-friendly methods, silica extraction from agricultural waste needs to be burnt first which can cause CO_2 gas pollution and environmental issues because of the major content of hydrocarbons in lignocellulose. Pyrophyllite rock is largely a raw material that is neglected and is available in large quantities in nature but silica extraction from pyrophyllite rock has not been reported yet [16]. This is because these minerals are rarely formed in a pure state such as kaolinite, but instead are mixed with quartz, kyanite, sericite, and diaspora with a certain composition which affects their properties and behavior [16]. This fact makes the extraction of silica from rock more challenging due to the high amount of silica content and the need for particular treatment compared to agricultural waste ash which is easy to extract but has little silica content. This study aims to compare the silica extraction process on Pyrophyllite rocks from Malang using the sol-gel method versus alkali fusion method.

2 Experimental

Pyrophyllite rock obtained from Sumbermanjing Wetan, Malang, Indonesia ($Al_2Si_4O_{10}(OH)_2$). While other chemicals were obtained with the following specifications, hydrochloric acid (HCl pa, 37%), sodium hydroxide (NaOH pellets p.a, Merck, 99%), Aquades, oxalic acid ($H_2C_2O_4.2H_2O$ p.a, Merck, 99%), and pH Indicator.

2.1 Silica Extraction Method

Silica powder was extracted using the sol-gel method and the alkaline fusion method. A total of 100 g of Pyrophyllite rock was prepared by immersion in 6 M HCl solution for 3 hours for decarbonisation and removal of impurity oxide compounds. Pyrophyllite powder was then washed until the pH was neutral, then dried in an oven at 110 ºC for 6 hours and ready to be used as a preparation for each method.

In the sol-gel method, 25 g of Pyrophyllite powder was added to 125 mL of 4 M NaOH solution and then refluxed at 100 ºC, 500 rpm for 9 hours. Whereas in the alkaline fusion method, as much as 25 g of Pyrophyllite powder is mixed with 30 g of solid NaOH then placed in a crucible and left for 30 minutes. The mixture was then calcined at 600 ºC for 1 hour and the solid obtained was pulverized with a mortar and dissolved in 250 mL of distilled water at 60 ºC, 500 rpm for 1 hour.

After being left to stand, each mixture of the two methods can be filtered and the filtrate is obtained in the form of Na_2SiO_3 solution. Then, the filtrate was added with 1 M HCl solution slowly until pH of 1 and kept for 24 hours. The filtrate was then dripped with 4 M NaOH solution to form a white gel in the pH range 7-8. The precipitate was kept overnight then filtered and dried in an oven at 110 °C for 6 hours. The obtained silica was refined and characterized using XRD and XRF instruments.

2.2 Characterization of Pyrophyllite and Silica

The X-ray diffraction patterns in the Pyrophyllite rock and silica were analyzed using X-Ray Diffraction Powder (XRD) PANalytical type E'xpert Pro. Samples were analyzed using XRD measurements through an angle of 2θ, range 10-90°, reading rate of 0.02°, 0.7 seconds, and using copper (Cu) as anode with wavelength (α) of 1.54 Å. While the analysis of the percent composition of silica and other oxides before and after treatment was determined using X-Ray Fluorescence (XRF) of the PANalytical brand Minipal 4 type.

3 Result and Discussion

The X-ray diffraction pattern analysis was carried out on Pyrophyllite rock samples both before and after treatment to determine changes in rock structure and crystallinity. The results of the X-ray diffraction patterns in each sample can be seen in Figure 1. The results of the XRD analysis of the initial pyrophyllite rock samples (as shown in Figure 1a) show a diffractogram pattern with specific and corresponding 2θ angle peaks, at 19.41°, 21.04°, 21.45°, 22.20°, 26.69°, 27.97°, 29.30°, 31.66°, 39.42°, 40.51°, 45.30°, 45.86°, 50.01°, 54.82°, 54.99°, 58.15°, 59.99°, 60.22°, 64.06°, 65.85°, 68.03°, 68.17°, 68.48°, 73.49°, dan 75.61° so it can be concluded that the diffractogram of the rock sample crystalline and compatible with database #PDF:00-900-8041 which is a diffractogram pattern of Pyrophyllite rock. Apart from the diffraction pattern of Pyrophyllite, a crystalline phase peak of impurity in the form of Quartz was found which is in accordance with database #PDF:00-901-3321. Apart from Pyrophyllite and quartz, these rocks also contain other metal oxides which can be identified based on the results of XRF analysis (as shown in Table 1).

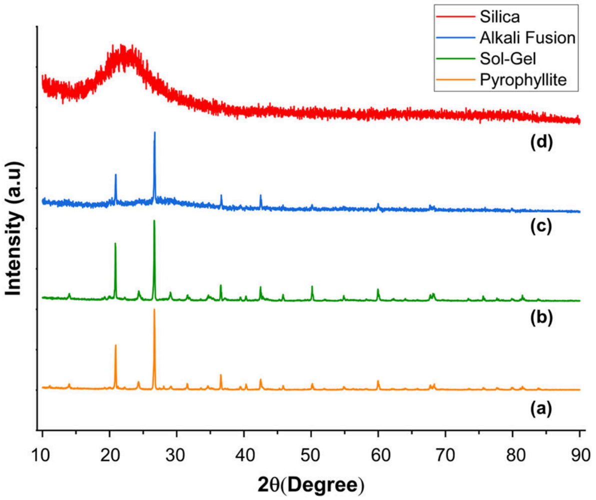

Fig. 1. X-Ray difraction pattern of, a) pyrophyllite, b) Sol-Gel residue, c) Alkali fusion residue, d) silica.

The X-ray diffraction pattern on pyrophyllite residue using the sol-gel method (as shown in Figure 1b) obtained a diffraction pattern almost identical to that of the initial pyrophyllite rock. Whereas in the pyrophyllite residue using the alkaline fusion method (as shown in Figure 1c), a different diffraction pattern was obtained in which several peak intensities decreased and some peaks coincided which indicated the presence of an amorphous phase that was formed. This can happen because the extraction process using the alkaline fusion method at 600 ºC can trigger the dihydroxylation reaction of the hydroxyl groups (Al–OH) in the alumina inter-layer, so that the alumino-silicate layer in pyrophyllite reacts more easily with base [16]. The appearance of the amorphous peaks left behind in the residue of the alkaline fusion method is due to the dissolving process of the alkaline fusion mixture with water still unable to extract the amorphous silica contained in the pyrophyllite as a whole. Thus, the process of extracting silica from rock is strongly influenced by 1) the structure and crystalline phase of the rock, 2) the calcination temperature, 3) the leaching and dissolving process of silica [8], [17]–[19].

Table 1. Comparing residue of pyrophyllite using sol-gel method versus alkali fusion method.

Components	Raw Material Pyrophyllite (wt%)	Residue (wt%)	
		Sol-Gel	Alkali Fusion
SiO_2	76.2	73.6	66.8
Al_2O_3	21.2	22.1	26.4
CaO	0.54	0.73	1.57
TiO_2	1.49	1.98	3.69
Fe_2O_3	0.37	0.44	1.10
V_2O_5	0.05	0.04	0.04
Cr_2O_3	0.08	0.06	0.07

The results of the XRD analysis of silica from Pyrophyllite rocks (as shown in Figure 1d) show an irregular (overlapping) diffractogram pattern that is dominantly widened in the range 2θ = 15 – 36º, with a peak angle of 2θ around 23º so it can be concluded that the diffractogram of the sample extracted is a pattern of amorphous silica (SiO_2). Based on the diffractogram pattern, no other high-intensity 2θ peaks were found so that the obtained silica (SiO_2) is a pure compound with very low impurities. In generally, the impurity is NaCl or other salt with a crystalline phase which is formed during the deposition of silica, so the separated silica has been washed properly without leaving much salt/impurity. These results were corroborated by XRF analysis that silica extracted from pyrophyllite rocks obtained with a purity of 99.3% (as shown in Table 2).

The results of XRF analysis of pyrophyllite rocks (as shown in Table 1) show that several oxide compounds with the highest percentage is silica (SiO_2), which is 76.2%, so the Pyrophyllite rock has enormous potential for silica extraction with high yield. Pyrophyllite rock has a high silica content but has a predominantly crystalline phase so it needs certain treatment before the extraction process. This presents a challenge during the research process. Following the extraction of silica using both the sol-gel and alkali fusion methods, an analysis was conducted to compare the content of oxide compounds before and after treatment. The most effective silica extraction method was identified by reducing silica percentage in pyrophyllite rock. A comparison between the composition of the residual pyrophyllite from the sol-gel and alkali fusion methods (as shown in Table 1) reveals that the alkali fusion technique yields more extraction results than the sol-gel method. The highest silica yield achieved in this study was with the alkali fusion method, reaching 10%wt compared to the sol-gel method which was only 3%wt.

The silica extraction process is carried out using the alkaline fusion method with a calcination temperature of 600ºC which can change the Pyrophyllite rock structure through dehydroxylation of the alumina inter-layer structure. Thus, Pyrophyllite rocks becomes activated and more reactive towards reactions with bases [16]. It was evidenced by changes in the shape and color of Pyrohyllite rocks which originally red in color to become blue-green crystals after calcination (as shown in Figure 2).

Fig. 2. a) pyrophyllite (raw material), b) pyrophyllite powder, c) calcined-alkali fusion pyrophyllite, d) precipitated silica from Pyrophyllite.

Table 2. Silica extraction from pyrophyllite.

Components	**Extracted Product from Pyropyllite (wt%)**
SiO_2	99.3
K_2O	0.08
CaO	0.30
TiO_2	0.18
Fe_2O_3	0.04
V_2O_5	0.01
Cr_2O_3	0.03

3.1 Perspectives in Silica Extraction

Extraction using alkaline and sol-gel fusion methods on these pyrophyllite rocks tends to be less than optimal when compared to extraction from plant ashes and other rocks. In silicate rocks, the silica content varies from 50-70 wt% with a dominant crystalline phase [1], [20], whereas in plants it is generally dominated by lignocellulose with an ash mass of no more than 15 wt%. This plant ash has a silica content that varies between 10-80%, depending on the type of plant [4], [21]. Rock extraction has the advantage in terms of high amount per unit weight but requires thermal treatment to change the crystalline phase of the silicate component. On the other hand, extraction of silica from plant ash has ease in terms of extraction because it's amorphous phase of silica but small amount of silica is obtained. In terms of Eco-friendly methods, it's important to note that extracting silica from agricultural waste necessitates initial combustion, a process that can result in CO_2 gas emissions and environmental concerns. Conversely, the extraction of silica from rocks is more environmentally friendly but requires a lot of energy in thermal treatment to change the crystalline silica phase.

Evaluation to increase the effectiveness of silica extraction from rocks can be carried out by 1) increasing the calcination temperature to damage the pyrophyllite structure so that a more dominant amorphous phase is formed according to the thermal decomposition temperature, 2) optimizing the leaching process to minimize the amount of impurities by increasing the acid concentration, 3) modifying the method sol-gel with thermal treatment first.

4 Conclusion

Silica has been extracted from pyrophyllite rocks by sol-gel or alkaline fusion methods. The maximum silica yield obtained in this research was through the alkali fusion method, reaching 10 wt% compared to the sol-gel method which was only 3 wt%. The silica obtained has a purity of 99.3%. The amount of silica that can be extracted is affected by the changes in the crystalline silica phase during the calcination process. For further research, it is highly recommended to increase the calcination temperature until the quartz/silica crystalline phase can change to an amorphous phase, thereby increasing the reactivity of silica towards bases and obtaining more optimum extraction results.

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