

Biobeneficiation of Langkat quartz sand by using indigenous *Aspergillus niger* fungus

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Abstract

Purpose. This research aims to characterize the Langkat quartz mineral, especially its impurities, and to study the effectiveness of fungal-based leaching methods to purify the mineral in order to improve the quartz quality for high-tech industrial applications.

Methods. Quartz was firstly analyzed to identify the mineral and chemical impurities. Quartz purification and beneficiation was performed by direct bioleaching using live indigenous *Aspergillus niger*, indirect bioleaching using metabolic lixiviant of the fungus, and chemical leaching using analytical grade oxalic acid.

Findings. The mineral composition of the Langkat quartz deposit is dominated by quartz mineral (93%) with minor amounts of orthoclase feldspar (KAlSi₃O₈, 5%) and calcite (CaCO₃, 2%). The chemical composition comprises 98.1% SiO₂ with metal impurities of 0.8% Fe₂O₃, 0.29% Al₂O₃, 0.03% NiO, 0.028% Cr₂O₃ and 0.063% CuO, indicating that quartz is still not enough for advanced material production industry. The bioleaching process removes up to 98% of iron (Fe₂O₃) from the original quartz sample, and completely removes other metals within eight days of the process by direct bioleaching and eight hours by indirect bioleaching. The content of Fe₂O₃ and other metals in the treated quartz meets the specifications of high purity quartz ($\leq 0.05\%$) for advanced material production industry. Meanwhile, chemical leaching using 0.2 M oxalic acid removes 96.9% of iron and 92.8% of aluminium.

Originality. Comparison of the bioleaching potential of present indigenous *Aspergillus niger* with some of the previous studies shows that this strain has a higher ability to remove metal impurities from quartz in a much shorter processing time (8 hours instead of weeks or months) than most of the previously published microorganisms.

Practical implications. The experimental result of this research provides significant potential for using a fungus-based purification approach to obtain high-purity quartz to be used in a high-value-added modern commercial product.

Keywords: high-purity quartz, indigenous Aspergillus niger, fungal metabolite, oxalic acid, metal impurities

1. Introduction

Quartz is a pivotal raw material for producing high-purity quartz, which is an essential substance for many advanced technology industries such as the semiconductor, optical fiber and photovoltaic industries [1]. In contrast, low-grade quartz sand is only used to make ceramics, glassware, and construction materials [2]. For high-tech industry applications, the quartz needs to have sufficient chemical purity properties, as shown in Table 1. Quartz is a common and abundant mineral in the Earth's crust, and naturally occurring low-impurity quartz is a rare and valuable mineral [3]. The minerals impurities in quartz sand are commonly feldspar, hematite, and goethite, while Al, Fe, Mg, Ca, Li, K, Na, B, Ti, H, Cr, Mn, and Ni are the main elemental impurities [4], [5] Iron and aluminium are the most undesired elemental impurities in quartz due to their detrimental effect on the production of high-tech end products and are difficult to completely remove.

It is concluded that different purification methods deal with different types of impurities based on the mineralogical study, their quantities and their distribution in the sand. Despite the fact that there are various purification techniques to reduce impurity amount in quartz, the characteristics of the mineral are quite essential to obtain acceptable purified quartz in the market [1], [6], [7]. Therefore, it is highly recommended to develop a purification process based on the characteristics of the impurities in the quartz sand.

Langkat Regency, located in North Sumatra Province, Indonesia (Fig. 1), has huge and important natural quartz resource. Nevertheless, quartz deposits are located in a region with poor infrastructure, mined by local miners using low-tech mining techniques, and cannot maintain the quality of their products. The Langkat quartz deposit is an economically interesting raw material, as evidenced by the high silica content (98.1%). It can be used directly as a bulk product for the glass or foundry industry with low economic benefit due to its low price.

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Received: 14 June 2023. Accepted: 11 September 2023. Available online: 30 September 2023

Mining of Mineral Deposits. ISSN 2415-3443 (Online) | ISSN 2415-3435 (Print)

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Tuble 1. High grade quart, specification in the global market					
Type of quartz	SiO ₂ minimum, (%)	Maximum element impurities, (%)	Market size, (m tpa)	Prices, (\$/tonne)	
Clear glass grade	99.50	0.50	> 70	30	
Optical glass grade	99.80	0.20	2	150	
Low-grade high purity quartz	99.95	0.05	0.75	300	
Medium-grade high purity quartz	99.99	0.10	0.25	500	
High-grade high purity quartz	99.997	0.003	< 0.10	5000	





Figure 1. Sampling location of quartz in Tambang Lawan village, Bahorok district, Langkat Regency, North Sumatra Province. Source: Google map

Therefore, the quartz properties should be improved by removing undesired metal impurities, especially iron and aluminium, to obtain suitable raw material for higher value industries. Upgrading the technical specification of Langkat quartz will open up its potential use in high-tech industries and significantly increase its production for local and global trade.

Several upgrading methods for purifying quartz by partially removing the iron are available, such as grinding [8], flotation [9], [10], and heavy-media separation or magnetic separation [11]. Nevertheless, these methods rarely reduce iron and other metal impurities to sufficient levels accepted by the market [7]. Certain effective techniques, including chlorination roasting [12], [13] high-temperature calcination, microwave heating [14], [15] ultrasonic treatment [16], [17] water quenching [18], and acids leaching [2] are expensive and have a large environmental impact.

The use of weak organic acids as leaching agents in mineral purification poses exciting potential. The most promising organic acid is oxalic acid due to its ability to reduce metals and complex formation [19]-[22]. Organic acids dissolve iron oxide by attacking H⁺ ions on the mineral solid, stabilizing them by forming soluble chelates and complexes in solution. The mining industries generally use chemicalbased oxalic acid, but naturally occurring oxalic acid is ubiquitous and microbes produce this low molecular weight organic acid. Oxalic acids can be produced by fermentation process of filamentous fungi, including soil-borne fungi such as Aspergillus and Penicillium [23]-[25]. Aspergillus niger is known as the best organic-acid producer [26], [27]. To obtain the best fungus, it is necessary to isolate indigenous fungus with better capabilities to increase the removal of metal impurities from quartz due to the higher adaptability of the fungus to the mineral. In addition, the dissolving ability of each type of fungus can be optimized by adjusting the environmental conditions (acidity, temperature), nutrient composition of the substrate, and incubation time [28].

This biotechnological method using fungal metabolites to remove metal impurities is less complex, cheaper, easy to purify, and produces less waste. Previous laboratory experiments verify that bacteria and fungi can leach iron from kaolin, felspar, and quartz [29]-[31]. However, no studies have been reported on fungal-based purification of quartz to remove iron and other metals from Langkat quartz. The effectiveness of microbiological leaching depends on the mineralogical characteristics of the raw material and metal binding properties [31], [32]. The objective of the present research is to characterize Langkat quartz, focusing on the development of bioleaching methods to purify quartz to high grades. This study also compares the effectiveness of the bioleaching method with chemical leaching by using pure chemical oxalic acid.

2. Methods

Purification of Langkat quartz began with quartz sample preparation, isolation of native *Aspergillus niger* (*A. niger*) from the quartz sample, followed by bioleaching and chemical leaching experiments (Fig. 2).



Figure 2. Process flow diagram of quartz purification

Langkat quartz was first characterized by its particle size distribution, as well as its mineralogical and chemical properties. The 208-295 nm mineral sample was then used for bioleaching, and a chemical leaching experiment using oxalic acid. In order to perform bioleaching experiment, indigenous fungi were isolated and characterized from Langkat quartz using potato dextrose agar.

2.1. Mineral sample

The quartz sand sample was taken from quartz deposit in Langkat, North Sumatra (Fig. 1). The samples were taken from eight different pits in the mined area to represent the actual deposits as accurately as possible. Samples were mixed and homogenized to prepare a representative sample for mineralogical, chemical, and biobeneficiation purposes. The particle size distribution of the bulk sample was determined by wet vibrating sieving. The sample was then sent for detailed mineralogical study using X-ray diffraction (XRD). Chemical composition of the samples was analyzed using X-ray fluorescence (XRF) of Panalytical Philips spectrometer.

2.2. Isolation of indigenous Aspergillus niger

The filamentous fungi *A. niger* used in this research was isolated from a quartz mineral sample. A total of four sand samples from different sampling points in the Langkat quartz sand area were taken aseptically, labeled and placed in sterilized ziplock bags. The collected samples were stored under normal storage conditions and brought to the laboratory on the same day for microbiological testing. The mineral was heated for 15 min at 80°C to eliminate the nonspore-forming fungal species. To isolate and identify fungal strains, solid media of potato dextrose agar (PDA) was used. In order to eliminate bacterial growth, 1% of chloramphenicol was added to the PDA.

Fungal isolation was performed by spreading the mineral suspension to the PDA and incubating at 30°C for 5-10 days. *A. niger* colonies were identified by their characteristics on PDA at 30°C; they were woolly, initially white and then turning black with black conidiospores. Macroscopic characteristics of *A. niger*, including colony growth, color, texture, and conidia, were observed after 10 days of inoculation. A single colony, supposed to be *A. niger*, was isolated for morphological characterization under a light microscopes [33]. The colonies were then purified on PDA plates. This identification was finally confirmed by a polymerase chain reaction (PCR) analysis.

2.3. Metal bioleaching by direct and indirect methods

Before the direct bioleaching experiment, 20 g of quartz samples were added to 500 ml Erlenmeyer flask containing 200 ml of a medium consisting of glucose 40 g/l, KH₂PO₄ 0.5 g/l, NaNO₃ 1.5 g/l, MgSO₄·7H₂O, 0.025 g/l, KCl 0.025 g/l and yeast extract 1.6 g/l. The pH of the medium was adjusted with NaOH 2 M to obtain pH 6.2, buffered with Tris 1 M, then sterilized for 30 min at 121°C. After cooling at room temperature, the flasks were inoculated with 2 ml of spore suspension $(5 \cdot 10^6 \text{ spores/ml})$, then incubated on a rotary shaker at 250 rpm at room temperature (23-25°C) for 10 days. The control flask was without the fungus that was incubated under similar conditions. After bioleaching experiments, the culture liquid was filtrated to separate the solution from the solid fraction. All experiments were performed in triplicates and the reported values were the average. The concentration of oxalic acid and leached metal ions (iron, aluminium, nickel, chrome and cobalt) in the solution was measured and determined every day for 8 days; and metal removal rates were calculated.

An indirect bioleaching experiment was conducted using metabolite-lixiviant produced by *A. niger*. To collect oxalic acid-containing metabolite, *A. niger* was cultivated in a 11 Erlenmeyer flask containing 500 ml of the previously mentioned quartz-free medium. After 8-days, the medium was filtrated, and the fungi-free supernatant was used as a leaching agent for the quartz purification process. Indirect bioleaching of 20 g quartz samples was performed using

200 ml of fungus metabolite in a 500 ml stirrer reactor. The leaching process was carried out at room temperature (23-25°C) at 250 rpm for 8 hours. Samples were taken at 1-hour intervals to measure the concentration of metal ions in the solution. All experiments were conducted in triplicates, reported values were the average.

2.4. Chemical leaching

To compare the effectiveness of the fungal leaching technique, a chemical leaching testing using pure chemical oxalic acid was performed in a 500 ml stirrer reactor. A 20 g quartz sample was added to a reactor with 200 ml of 25.2 g/l (0.2 M) pure oxalic acid solution, then stirred at 250 rpm for 8 hours at room temperature. A 1 ml of liquid sample was collected at 1-hour intervals to monitor the extracted metals during the leaching process. After experimental testing, the samples were filtrated, and the residue was washed with reverse osmosis water. The residue and leached solution were analyzed for metal content.

2.5. Analytical measurement

Metal ion concentrations in solution samples generated and collected during leaching experiments were determined using an Inductively Coupled Plasma (ICP) OES Thermo Fisher ICAP 7000 instrument. The amount of oxalic acid produced by *A. niger* was measured by High-Performance Liquid Chromatography (HPLC) using a Rezex ROA Organic Acid column (Phenomenex) coupled to a UV detector at 210 nm. The column was eluted with 0.0025 M H₂SO₄ at a 0.5 ml/min flow rate.

3. Results and discussion

3.1. Characterization of the Langkat quartz mineral

The quartz mined from the Langkat deposit was yellowish-brown in color because of the presence of iron and coatings of clay on the quartz sand. The XRD pattern of the quartz sample (Fig. 3) has revealed that quartz mineral (93%) is associated with an appreciable amount of orthoclase feldspar (K(Al, Fe)Si₂O₈ 5%) and calcite (CaCO₃ 2%).



Figure 3. XRD pattern of Langkat quartz sample: Q-quartz; O-orthoclase; C-calcite

The quantitative chemical composition of Langkat quartz samples is presented in Table 2. The quartz sample contained silicon oxide (SiO₂) 98.1%, as well as metal oxide impurities of Fe₂O₃ – 0.8% and Al₂O₃ – 0.29% that present in notable

quantities as the main impurities. The sample also contained 0.03% of NiO, 0.028% of Cr_2O_3 , and 0.063% of CuO. Iron oxides were the major component of iron in the sand, while orthoclase feldspar was the main component of aluminium.

Diameter (µm)	%	Metal oxide	%
> 495	0.20	SiO ₂	98.10
295-495	8.56	Fe2O ₃	0.80
208-295	55.66	Al ₂ O ₃	0.29
147-208	31.84	NiO	0.03
104-147	2.67	Cr_2O_3	0.028
74-104	1.05	CuO	0.063
< 74	0.02	LOI	0.69

Table 2. Size distribution and chemical composition of quartz sample

The quartz sand particle size distribution is presented in Table 2. The highest percentage of sand size distribution was in the range of 295-208 μ m, therefore this particle size was used in the experimental leaching process.

3.2. Indigenous Aspergillus niger

The quartz samples from the Langkat pit are characterized by a lot of fungal species, especially *A. niger*. This fact indicates that the fungi dominante and represent an active microbial community in this ecosystem. PCR analyses confirmed that the isolated fungus is *A. niger* strain An-S167. Colony color, morphology and vegetative hypha characteristics of fungus are depicted in Figures 4 and 5.



Figure 4. A 4-day-old colony of A. niger in Potato Dextrose Agar (a) with the black conidia in the centre of colony which spread outwards resulted in slightly raised and rough colony (b)



Figure 5. Microscopic characteristics of Aspergillus niger under light microscope indicating the radiate phialides, globose conidia, unbranced and non-septate conidiophore

White colonies were observed after 4 days, although mycelia sporulation began in the centre of several colonies (Fig. 4a). From the 5th to the 10th day, sporulation that began from the colony center, intensified; the colony centre became black after 10 days (Fig. 4b) due to the colour of conidia. Sporulating mycelia extended to a white border around the colony, indicated by a small amount of black mycelia at the border. The generative hyphae of *A. niger* have developed a reproductive structure including conidiophore, phialides, vesicle and conidia (Fig. 5).

3.3. Removal of metal impurities by bioleaching

In this research, metal ions leached from quartz were released into the solution, indicating the mineral dissolution resulting in quartz beneficiation. The main goal of fungal leaching was to obtain treated quartz with as little metal content as possible compared to untreated one. In particular, the targeted grades were maximum Fe_2O_3 and Al_2O_3 concentrations below 0.05% to produce high-purity quartz for the high-tech industry. Thus, the process required a minimum extraction yield or iron and aluminium removal of 94%.

Direct bioleaching results show that 97.9% of Fe₂O₃ can be leached from the mineral to achieve an ultimate concentration 0.017% of Fe₂O₃ in the treated quartz (Table 3). In addition, the bioleaching process removed 100% of aluminium, chrome, nickel and copper within 8 days of leaching time (Fig. 6a). Removal of iron and aluminium begins in the first 2 days of incubation, then increases rapidly from day 3 to day 7, and finally yields maximum removal after 8 days.

Table 3. Removal of metal impurities from quartz by direct and indirect bioleaching

Matal	Metal conc	Metal concentration, (%)				
ovido	Original	After				
Oxide	sample	bioleaching				
Direct bioleaching						
Fe ₂ O ₃	0.80	0.017 ± 0.0005	97.9 ± 0.0007			
Al ₂ O ₃	0.29	nd	100			
NiO	0.03	nd	100			
Cr ₂ O ₃	0.028	nd	100			
CuO	0.063	nd	100			
Indirect bioleaching						
Fe ₂ O ₃	0.80	0.015 ± 0.0005	98.1 ± 0.0007			
Al ₂ O ₃	0.29	nd	100			
NiO	0.03	nd	100			
Cr ₂ O ₃	0.028	nd	100			
CuO	0.063	nd	100			

nd - not detected

In this direct bioleaching process, fungi started to produce oxalic acid in the first 2 days of incubation and yielded a maximum 25.2 g/l (0.2 M) concentration after 7 days of the process using an initial concentration 40 g/l of glucose in the medium (Fig. 6a). Compared to Ilgar & Torma [34], who produced 5 g/L of oxalic acid in 1.51 bioreactor for 10 days, this work yielded more than fivefold increase in oxalic acid production. The current work also had a relatively better yield than Walaszczyk et al. [27], who reported that *A. niger* can produce oxalic acid up to 64.3 g/l, which is achieved after 10 days of cultivation using initial 125 g/l concentration of sucrose in the medium.

Iron and aluminium ions were leached into the solution during the 8-day bioleaching process. It was also observed that the metal leaching rate increased gradually as the concentration of oxalic acids in the solution increased.



Figure 6. Production of oxalic acid (g/l) and Fe-Al removal (%) by direct bioleaching (a) and indirect bioleaching process (b)

The oxalic acid concentration remained stable after 7 days and the metal leaching rate was also stable. The clear and strong relationship between the oxalic acid concentration and the metal leaching rate of Fe and Al suggests that the Fe and Al leaching reaction is catalyzed by oxalic acid released into the liquid phase. It is observed that the most leached Fe and Al ions correspond to the highest production of oxalic acid by fungi.

The *A. niger* produces oxalic acid and enzymes to degrade and leach minerals [35]. The fungus destroys the mineral structure and leaches out elements needed for metabolism and structural purposes. This is particularly essential for Fe and Al ions. Moreover, oxo-anions in oxalic acid can capture impurities bound to the surface of quartz particles because they are more electronegative than those in quartz.

The following are the reactions of iron with oxalic acid [35]:

$$Fe_2O_3 + 6H_2C_2O_4 \rightarrow 2Fe(C_2O_4)_3 + 6H^+ + 3H_2O;$$
 (1)

$$2Fe(C_2O_4)_3 + 6H^+ + 4H_2O \rightarrow 2FeC_2O_4 \cdot 2H_2O + 3H_2C_2O_4 + 2H_2O; (2)$$

$$Fe_2O_3 + 3H_2C_2O_4 + H_2O \rightarrow 2FeC_2O_4 \cdot 2H_2O + 2CO_2;$$
 (3)

$$Fe^{3+} + [C_2O_4]^{2-} \rightarrow [Fe(C_2O_4)]^+;$$
 (4)

$$[Fe(C_2O_4)]^+ + [C_2O_4]^{2-} \to [Fe(C_2O_4)_2]^-;$$
(5)

$$[Fe(C_2O_4)2]^{-} + [C_2O_4]^{2-} \to [Fe(C_2O_4)_3]^{3-}.$$
 (6)

Meanwhile the chemical reaction below is oxalic acid with aluminium [21]:

$$2Al_{2}O_{3} + 3H_{2}C_{2}O_{4} \rightarrow 2Al(C_{2}O_{4})_{3}^{3-} + 4H_{2}O + Al_{2}(C_{2}O_{4})_{3} \cdot 2H_{2}O + 6H^{+}.$$
 (7)

The result of direct bioleaching in the current work is quite promising; however, it was a time-consuming process. The indirect bioleaching experiment was intended to reduce processing time, i.e., reduce the leaching time to a few hours instead of days. Indirect bioleaching is the bioleaching of quartz using metabolite-lixiviant generated by *A. niger*. The metabolites comprised loose slime and oxalic acids that are solely responsible for metal leaching. The percentage of iron and other metal leaching from quartz by the metabolite alone in the absence of active spores is presented in Table 3 and Figure 6b. It has been observed that indirect bioleaching can remove metals (iron, aluminium, nickel, chrome and copper) in the same yields as direct bioleaching, but in a much shorter time, i.e., entirely within 7 hours only. The experimental conditions were sufficient to produce high purity quartz sands with the desired minimum impurity content value $\leq 0.05\%$ for feeding high-tech industry. Although concentrations of other metals were zero (not detected) in the treated ore after direct bioleaching, this result does not meet the standards for more advanced technology applications. Fibre optic application requires a total metal content below 30 ppm; meanwhile, the pure silicon production should be below 1 ppm. Figure 7 presents the quartz sand color before and after the bioleaching process. It can be seen that the color has changed significantly from yellowish brown to whiter due to reduced iron content.



Figure 7. Quartz sand: (a) before bioleaching process; (b) after bioleaching process

3.4. Removal of metal impurities by chemical leaching

The experiment used pure oxalic acid at the same concentration as the amount of oxalic acid produced by *A. niger* during the fungal leaching process (25.2 g/l). The results in Table 4 and Figure 8 show that chemical leaching results in lower metal removal than fungal leaching.

Table 4. Removal of metal impurities from quartz by chemical leaching for 8 hours

Metal — oxide	Metal con	Metal concentration (%)		
	Original	After chemical	% removal	
	sample	leaching		
Fe ₂ O ₃	0.80	0.025 ± 0.0005	96.9 ± 0.0007	
Al ₂ O ₃	0.29	0.021 ± 0.0005	92.8 ± 0.0002	
NiO	0.03	nd	100	
Cr ₂ O ₃	0.028	nd	100	
CuO	0.063	nd	100	

nd – not detected



Figure 8. Iron and aluminium removal from quartz by chemical leaching

The dynamics of metal removal curve are almost the same, but give lower maximum removal values -96.9% and 92.8% for iron and aluminium, respectively (Table 4, Fig. 8). In the current experiment, 0.025% of Fe₂O₃ and 0.021% of Al₂O₃ were still left in the treated quartz. This chemical process was not capable to remove all non-quartz minerals. The ability of oxalic acids in chemical leaching is intrinsic and does not depend on fungus metabolism. This result suggests that the active metabolism of *A. niger* positively enhances quartz purification.

In another experiment conducted on Turkey quartz sand [36], fungal leaching of Fe₂O₃ by A. niger resulted in 47.70% iron removal from the mineral in 21 days of the process. The Fe₂O₃ content decreased from 0.315 in the original sample to 0.164% in the bioleached quartz. It has been revealed that this fungus strain is not capable of removing iron impurities from quartz minerals compared to chemical leaching. The fungal strain of A. niger used in these experiments was a readily available stock pure culture from the laboratory and not isolated from the original quartz sand. The present study confirms that the indigenous fungal strain had a higher ability to remove iron from quartz and did so almost three times faster in 8 days. Moreover, indirect bioleaching using a metabolite lixiviant of indigenous A. niger can remove 98% of iron from quartz in a much shorter leaching time of 7-8 hours.

Fungal bioleaching in the current study resulted in more effective iron removal compared to bacteria. In the experiment conducted by Suba and Styriakova [31], bioleaching using heterotrophic bacteria removed 30-50% of the Fe content from three types of quartz samples with different mineralogical properties in 83 days of the process. The original quartz samples comprised 85.8-96.1% of SiO₂, 0.26-1.03 of Fe₂O₃ and 1.71-7.71% of Al₂O₃. Štyriaková et al. [37] also reported that the metabolic activities of *Bacillus cereus* could remove only 17% of iron and 5% of aluminium from quartz after 3 months of bioleaching. The comparison of the bioleaching ability of indigenous *A. niger* with some previous studies shows that this strain has a higher ability to remove metal impurities than most previously mentioned microorganisms.

4. Conclusions and suggestions

According to XRF analysis, mineral characterization has revealed that the quartz from Langkat is mainly composed of 98.1% of SiO₂, 0.8% of Fe₂O₃ and 0.29% of Al₂O₃. The XRD analysis has revealed that orthoclase feldspar and calcite minerals are also identified in the quartz. The large amount of Fe₂O₃ contributed to the yellowish-brown quartz color. After bioleaching, the quartz color became much whiter due to the reduced iron content.

The current work demonstrates the effective role of indigenous fungi in leaching iron and aluminium impurities from Langkat quartz. When comparing quartz purification by fungal leaching and chemical leaching, fungal leaching shows better results. Both direct fungal leaching and indirect mechanism play a great role in quartz biobeneficiation. The Fe₂O₃ content in quartz reduces from 0.81 to 0.018%, and other metal oxides of Al, Ni, Cu and Cr are removed completely. Meanwhile, after chemical leaching using 0.2 M oxalic acid, 0.025% of Fe₂O₃ and 0.021% of Al₂O₃ still remained in the treated quartz. The use of fungi for removing metal impurities may be a reliable technique for increasing the silica content of quartz and its commercial value. The reported results support the potential of fungal leaching methods for quartz purification, adequate for the advanced materials industry.

These bioleaching processes have three advantages:

(a) the low concentrations of oxalic acid generated and utilized in the bioleaching process pose less of a risk to the environment;

(b) the relatively short time (7-8 hours) needed to complete the indirect bioleaching process with better results;

(c) the leaching cost can be quite significant since it is carried out at room temperature (25-27°C). All the advantages mentioned above can facilitate its commercial applications.

By appropriately controlling biological processes and optimizing influencing factors such as pulp density, medium nutrition, biomass concentration and sand particle size, possibilities to enhance purification of the quartz are definitely closer to achieving the highest grade of high purity quartz (Fe₂O₃ < 0.003%).

Acknowledgements

The authors express their sincere grattitude to the Local Government and Industrial Office of Langkat Regency, Indonesia, for their assistance in collecting the necessary samples. They also acknowledge the Center for Testing of Mineral and Coal, Ministry of Energy and Mineral Resources for providing facilities and support in this work.

References

- Medjahed, S., Kheloufi, A., Bobocioiu, E., Kefaifi, A., Kerkar, F., & Lebbou, K. (2022). Quartz ore beneficiation by reverse flotation for silicon production. *Silicon*, (14), 87-97. <u>https://doi.org/10.1007/s12633-020-00790-x</u>
- [2] Khalifa, M., Ouertani, R., Hajji, M., & Ezzaouia, H. (2019). Innovative technology for the production of high-purity sand silica by thermal treatment and acid leaching process. *Hydrometallurgy*, (185), 204-209. <u>https://doi.org/10.1016/j.hydromet.2019.02.010</u>
- [3] Götze, J. (2009). Chemistry, textures and physical properties of quartz geological interpretation and technical application. *Mineralogical Magazine*, (73), 645-671. <u>https://doi.org/10.1180/minmag.2009.073.4.645</u>
- [4] Pathirage, S.S., Hemalal, P.V.A., Rohitha, L.P.S., & Ratnayake, N.P. (2019). Production of industry-specific quartz raw material using Sri Lankan vein quartz. *Environmental Earth Sciences*, (78), 1-13. <u>https://doi.org/10.1007/S12665-019-8060-3</u>
- [5] Vatalis, K.I., Charalampides, G., Platias, S., & Benetis, N.P. (2014). Market developments and industrial innovative applications of high purity quartz refines. *Procedia Economics and Finance*, (14), 624-633. <u>https://doi.org/10.1016/S2212-5671(14)00751-5</u>
- [6] Huang, H., Li, J., Li, X., & Zhang, Z. (2013). Iron removal from extremely fine quartz and its kinetics. *Separation and Purification Technology*, (108), 45-50. <u>https://doi.org/10.1016/j.seppur.2013.01.046</u>
- [7] Pan, X., Li, S., Li, Y., Guo, P., Zhao, X., & Cai, Y. (2022). Resource, characteristic, purification and application of quartz: A review. *Minerals Engineering*, (183), 107600. <u>https://doi.org/10.1016/J.MINENG.2022.107600</u>
- [8] Kohobhange, S.P.K., Manoratne, C.H., Pitawala, H.M.T.G.A., & Rajapakse, R.M.G. (2018). The effect of prolonged milling time on comminution of quartz. *Powder Technology*, (330), 266-274. <u>https://doi.org/10.1016/j.powtec.2018.02.033</u>
- [9] Rohem Peçanha, E., da Fonseca de Albuquerque, M.D., Antoun Simão, R., de Salles Leal Filho, L., & de Mello Monte, M.B. (2019). Interaction forces between colloidal starch and quartz and hematite particles in mineral flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, (562), 79-85. https://doi.org/10.1016/j.colsurfa.2018.11.026
- [10] Yang, L., Li, W., Li, X., Yan, X., & Zhang, H. (2020). Effect of the turbulent flow pattern on the interaction between dodecylamine and quartz. *Applied Surface Science*, (507), 145012. <u>https://doi.org/10.1016/j.apsusc.2019.145012</u>
- [11] Yin, W., Wang, D., Drelich, J.W., Yang, B., Li, D., & Zhu, Z. (2019). Reverse flotation separation of hematite from quartz assisted with

magnetic seeding aggregation. *Minerals Engineering*, (139), 105873. https://doi.org/10.1016/j.mineng.2019.105873

- [12] Lin, M., Lei, S., Pei, Z., Liu, Y., Xia, Z., & Xie, F. (2018). Application of hydrometallurgy techniques in quartz processing and purification: A review. *Metallurgical Research Technology*, (115), 303. <u>https://doi.org/10.1051/metal/2017105</u>
- [13] Zhang, Q.D., Li, X.L., Song, Y.S., & Zhou, G.Y. (2017). Experimental research on preparation technics of high-purity quartz material. *Key Engineering Materials*, (748), 17-21. https://doi.org/10.4028/www.scientific.net/KEM.748.17
- [14] Buttress, A.J., Rodriguez, J.M., Ure, A., Ferrari, R.S., Dodds, C., & Kingman, S.W. (2019). Production of high purity silica by microfluidic-inclusion fracture using microwave pre-treatment. *Minerals Engineering*, (131), 407-419. <u>https://doi.org/10.1016/j.mineng.2018.11.025</u>
- [15] Hou, Y., Liu, P., Hou, Q., Duan, H., & Xie, Y. (2017). Study on removal fluid inclusions in quartz sand by microwave explosion. *Nanoscience and Nanotechnology Letters*, 9(2), 151-154. <u>https://doi.org/10.1166/nnl.2017.2166</u>
- [16] Yang, C. (2018). Advanced purification of industrial quartz using calcination pretreatment combined with ultrasound-assisted leaching. *Acta Geodynamica et Geomaterialia*, 15(2(190)), 187-195. <u>https://doi.org/10.13168/AGG.2018.0014</u>
- [17] Yang, L., Li, X., Li, W., Yan, X., & Zhang, H. (2019). Intensification of interfacial adsorption of dodecylamine onto quartz by ultrasonic method. *Separation and Purification Technology*, (227), 115701. <u>https://doi.org/10.1016/j.seppur.2019.115701</u>
- [18] Li, F., Jiang, X., Zuo, Q., Li, J., Ban, B., & Chen, J. (2021). Purification mechanism of quartz sand by combination of microwave heating and ultrasound assisted acid leaching treatment. *Silicon*, (13), 531-541. <u>https://doi.org/10.1007/s12633-020-00457-7</u>
- [19] Du, F., Li, J., Li, X., & Zhang, Z. (2011). Improvement of iron removal from silica sand using ultrasound-assisted oxalic acid. *Ultrasonics Sonochemistry*, 18(1), 389-393. <u>https://doi.org/10.1016/j.ultsonch.2010.07.006</u>
- [20] Ibrahim, A.F.M., Seifelnassr, A.A.S., Al-Abady, A., El-Salmawy, M.S., & Abdelaal, A.M. (2022). Characterization and iron removal enhancement of El-Zaafarana white sand. *Mining, Metallurgy & Exploration*, (39), 2187-2198. <u>https://doi.org/10.1007/s42461-022-00667-0</u>
- [21] Li, J.S., Li, X.X., Shen, Q., Zhang, Z.Z., & Du, FH. (2010). Further purification of industrial quartz by much milder conditions and a harmless method. *Environmental Science & Technology*, (44), 7673-7677. <u>https://doi.org/10.1021/es101104c</u>
- [22] Vapur, H., Demirci, S., Top, S., & Altiner, M. (2015). Removal of iron content in feldspar ores by leaching with organic acids. *Proceedings of* the XVI Balkan Mineral Processing Congress, 761-766.
- [23] Li, Z., Bai, T., Dai, L., Wang, F., Tao, J., Meng, S., Hu, Y., Wang, S., & Hu, S. (2016). A study of organic acid production in contrasts between two phosphate solubilizing fungi: Penicillium oxalicum and Aspergillus niger. *Scientific Reports*, (6), 25313. <u>https://doi.org/10.1038/srep25313</u>
- [24] Liaud, N., Giniés, C., Navarro, D., Fabre, N., Crapart, S., Herpoël-Gimbert, I., Levasseur, A., Raouche, S., & Sigoillot, J.-S. (2014). Exploring fungal biodiversity: organic acid production by 66 strains of

filamentous fungi. *Fungal Biology and Biotechnology*, (1), 1. https://doi.org/10.1186/s40694-014-0001-z

- [25] Palmieri, F., Estoppey, A., House, G.L., Lohberger, A., Bindschedler, S., Chain, P.S.G., & Junier, P. (2019). Oxalic acid, a molecule at the crossroads of bacterial-fungal interactions. *Advances in Applied Microbiology*, (106), 49-77. https://doi.org/10.1016/bs.aambs.2018.10.001
- [26] Musial, I., Rymowicz, W., & Witkowska, D. (2006). Effect of span 20 concentration on oxalic acid production from post-refining fatty acids by Aspergillus niger XP. *Chemical Papers*, (60), 388-390. https://doi.org/10.2478/s11696-006-0070-4
- [27] Walaszczyk, E., Podgórski, W., Janczar-Smuga, M., & Dymarska, E. (2018). Effect of medium pH on chemical selectivity of oxalic acid biosynthesis by Aspergillus niger W78C in submerged batch cultures with sucrose as a carbon source. *Chemical Papers*, (72), 1089-1093. https://doi.org/10.1007/s11696-017-0354-x
- [28] Dusengemungu, L., Kasali, G., Gwanama, C., & Mubemba, B. (2021). Overview of fungal bioleaching of metals. *Environmental Advances*, (5), 100083. <u>https://doi.org/10.1016/j.envadv.2021.100083</u>
- [29] Qureshi, S.A., Qureshi, R.A., Sodha, A.B., Tipre, D.R., & Dave, S.R. (2018). Bioextraction dynamics of Potassium from feldspar by heterotrophic microorganisms isolated from ceramic and rhizospheric soil. *Geomicrobiology Journal*, 35(2), 127-131. https://doi.org/10.1080/01490451.2017.1338797
- [30] Roy, A., Singh, S.K., Banerjee, P.C., Dana, K., & Das, S.K. (2010). Bio-beneficiation of kaolin and feldspar and its effect on fired characteristics of triaxial porcelain. *Bulletin of Materials Science*, (33), 333-338. <u>https://doi.org/10.1007/s12034-010-0051-7</u>
- [31] Šuba, J., & Štyriaková, D. (2015). Iron minerals removal from different quartz sands. *Procedia Earth and Planetary Science*, (15), 849-854. <u>https://doi.org/10.1016/j.proeps.2015.08.136</u>
- [32] Arslan, V. (2019). Comparison of the rffects of Aspergillus niger and Aspergillus ficuum on the removal of impurities in feldspar by biobeneficiation. *Applied Biochemistry and Biotechnology*, (189), 437-447. <u>https://doi.org/10.1007/s12010-019-03029-7</u>
- [33] Senawong, T., Khaopha, S., Misuna, S., Bunyatratchata, W., Sattayasai, N., & Senawong, G. (2014). Histone deacetylase inhibitory activity and antiproliferative activity of the cultured medium of Aspergillus niger strain TS1. *Chiang Mai Journal of Science*, (41), 981-991.
- [34] Ilgar, E., & Torma, A.E. (1989). Fundamentals of microbial degradation of spodumene. Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, (76/89), 1-9.
- [35] Zeng, H., Lei, S., Liu, Y., & Zhang, F. (2012). Effect and complexation mechanism of complex ion in quartz purification by oxidation leaching. *Mining Research and Development*, (6), 67-70.
- [36] Arslan, V., & Bayat, O. (2009). Iron removal from Turkish quartz sand by chemical leaching and bioleaching. *Mining, Metallurgy & Exploration*, (26), 35-40. <u>https://doi.org/10.1007/BF03403416</u>
- [37] Štyriaková, I., Štyriak, I., Nandakumar, M.P., & Mattiasson, B. (2003). Bacterial destruction of mica during bioleaching of kaolin and quartz sands by Bacillus cereus. World Journal of Microbiology and Biotechnology, (19), 583-590. <u>https://doi.org/10.1023/A:1025176210705</u>

Біозбагачення кварцового піску Лангката із використанням місцевого грибка Aspergillus niger

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Мета. Дослідження характеристик кварцовового мінералу лангкат та вивчення ефективності методів вилуговування на основі грибків для очищення й подальшого покращення якості кварцу у високотехнологічних промислових застосуваннях.

Методика. Кварц був спочатку проаналізований для визначення мінеральних і хімічних домішок. Очищення та збагачення кварцу проводили шляхом прямого біологічного вилуговування із використанням живого місцевого грибка *Aspergillus niger*, непрямого біологічного вилуговування із застосуванням метаболічного вилуговувача грибка та хімічним вилуговуванням щавлевою кислотою аналітичного класу.

Результати. Встановлено, що у мінеральному складі кварцового родовища лангкат переважає кварцовий мінерал (93%) з незначною кількістю ортоклазового польового шпату (KAlSi₃O₈, 5%) та кальциту (CaCO₃, 2%). Визначено, що хімічний склад представлено 98.1% SiO₂ з домішками металів 0.8% Fe₂O₃, 0.29% Al₂O₃, 0.03% NiO, 0.028% Cr₂O₃ і 0.063% CuO, що вказує на те, що кварцу все ще недостатьно для промислового виробництва передових матеріалів. Виявлено, що у процесі біологічного вилуговування з вихідного зразка кварцу видаляється до 98% заліза (Fe₂O₃), а інші метали повністю видаляються протягом восьми днів шляхом прямого біологічного вилуговування та через вісім годин – шляхом непрямого біологічного вилуговування. Визначено, що вміст Fe₂O₃ та інших металів в обробленому кварці відповідає специфікаціям кварцу високої чистоти (≤ 0.05%) для промислового виробництва передових матеріалів, між тим, хімічне вилуговування із використанням щавлевої кислоти 0.2 М видаляє 96.9% заліза і 92.8% алюмінію.

Наукова новизна. Порівняння потенціалу біологічного вилуговування існуючого місцевого грибка Aspergillus niger з деякими із попередніх досліджень показує, що цей штам має більш високу здатність видаляти домішки металів з кварцу за набагато коротший час обробки (8 годин замість тижнів або місяців), ніж більшість мікроорганізмів, які були досліджені раніше.

Практична значимість. Експериментальний результат цього дослідження надає значний потенціал для використання підходу до очищення на основі грибків для отримання високочистого кварцу, який буде використовуватися в сучасному комерційному продукті з високою доданою вартістю.

Ключові слова: високочистий кварц, грибок Aspergillus niger, грибковий метаболіт, щавлева кислота, домішки металів