

Article

A Novel Open-System Method for Synthesizing Muscovite from a Biotite-rich Coal Tailing

Hamid Khoshdast ^{1,*}, Vahideh Shojaei ¹, Ahmad Hassanzadeh ², Tomasz Niedoba ^{3,*} and Agnieszka Surowiak ³¹ Department of Mining Engineering, Higher Education Complex of Zarand, 7761156391 Zarand, Iran; v.shojaei@uk.ac.ir² Independent Scholar, Am Apostelhof 7A, 50226 Frechen, Germany; a.hassanzadeh@gmx.de³ Department of Environmental Engineering, Faculty of Mining and Geoengineering, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland; asur@agh.edu.pl

* Correspondence: khoshdast@zarand.ac.ir (H.K.); tniedoba@agh.edu.pl (T.N.); Tel.: +48-126-172-056 (T.N.)

Abstract: According to the wide application of muscovite in various industries, many studies have focused on its fabrication. However, the process of its synthesis faces long-standing challenges mainly related to the elevated temperature and pressure ambient, together with time and cost-consuming processes. This research work aims at synthesizing muscovite through a straightforward and direct wet thermal oxidation of an ash sample produced from biotite-rich coal tailings. For this purpose, the lab ash powder was mixed with 35% H₂O₂ at the room temperature of 25 °C while stirring at 480 rpm. Then, the temperature was gradually raised to 80 °C, and the process ran for 180 min. The dried product and the raw lab ash were characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) methods. The XRD results indicated that the biotite was efficiently converted to the muscovite as the number of relevant peaks was significantly increased in the synthesized product's pattern. The SEM and FTIR results showed some structural changes, from pseudo-hexagonal in the starting material to amorphous pseudo-crystals in the synthetic product, as well as the growth of the product's crystals. The crystallographic study and lattice parameter calculations revealed that the starting material and product peaks matched to International Center for Diffraction Data (ICDD) reference patterns of 01-080-1110 and 01-082-2450 for the biotite and the muscovite, respectively. Moreover, the calculation of the mean crystallite size of the starting material and treated samples were obtained as 55 nm and 87 nm, respectively. Finally, according to the characterization properties of synthesized muscovite, the presented method was introduced as an effective technique. Therefore, we highly suggest it for further consideration and its development in future investigations.

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1. Introduction

Biotite and muscovite are two phyllosilicate minerals within the mica family that are commonly found in igneous and metamorphic rocks. Biotite has a small number of commercial uses, while muscovite has the greatest commercial value due to its special properties. Muscovite mineral is chemically inert, dielectric, elastic, flexible, hydrophilic, lightweight, reflective and refractive [1]. In addition, it is stable when exposed to electricity, light, moisture and extreme temperatures. Muscovite, either in the form of sheet or ground, is used in joint compound, paint, drilling mud, plastics, rubber, asphalt proofing and electronic devices [2].

The generalized chemical compositions for biotite and muscovite as a potassium-rich mica are $K(Mg,Fe)_3(AlSi_3O_{10})(OH,F)_2$ and $KAl_2(AlSi_3O_{10})(OH)_2$, respectively [2]. Biotite is not very resistant to weathering and transforms into clay minerals. In contrast,

muscovite is more resistant to weathering than biotite. In addition to weathering, the reduction/oxidation (redox) process is a pronounced mechanism resulting in mineral alterations. In the electrochemical series, Al^{3+} has a smaller redox potential ($E^\circ = -1.66 \text{ V}$) than Fe^{2+} ($E^\circ = -0.44 \text{ V}$) [3]. Therefore, Fe can be reduced and constituted by Al during the redox reaction. In the presence of a powerful oxidant such as hydrogen peroxide (H_2O_2), suitable conditions can be provided for $3\text{Fe}^{2+} \rightleftharpoons \text{Al}^{3+}$ substitution. This equilibrium can be postulated as the main substitution scheme during the synthesis process of muscovite from biotite. Other substitutions are $\text{Mg}^{2+}\text{Si}^{4+} \rightleftharpoons 2\text{Al}^{3+}$, $\text{K}^+\text{Al}^{3+} \rightleftharpoons \text{Si}^{4+}$ and $\text{H}_3\text{O}^+ \rightleftharpoons \text{K}^+$ [4].

In recent years, significant advances have been addressed in the field of clay material processing, which have mainly focused on the processing of clay materials from primary sources and the production of nano-clays and related compounds. Among them, the optimization of flotation [5–7] and leaching [8–10] methods have been considered more than other processing methods. Nano-clays have also been used mainly in combination with other organic and inorganic compounds in the form of composites to provide more beneficial physical and chemical properties [11–17]. In the case of muscovite, several synthesis procedures are described in the literature. These techniques can be categorized into four groups, including (I) reactions of phases of appropriate compositions, (II) recrystallization of decomposed natural mica, (III) alteration of natural minerals and (IV) structural modification. In the first method, a gel close to the requisite composition of muscovite is processed at 200–750 °C and 25–2000 atm for several days. The preparation methodology is mainly based on the work of Hamilton and Henderson [18]. The starting materials are a K salt, Al_2O_3 or $\text{Al}(\text{OH})_3$ and SiO_2 in the proper ratios [19–26]. Applying this method highly requires the appropriate and precise proportions of the primary components and excessive energy, temperature and pressure values. In this context, Jungo and Schreyer [27] reported a detailed description regarding the pressure–temperature stability of synthesizing boromuscovite ($\text{KAl}_2\text{BSi}_3\text{O}_{10}(\text{OH})_2$). In terms of method II, muscovite is resynthesized from its decomposition products. These materials are treated in a KOH solution at 400–650 °C and 100–700 atm for 12–100 h [28]. Synthesis through the third technique by the alteration of other minerals containing some of the necessary components has also been found to be fruitful by several investigators [29–32]. This method includes heating a mica mineral with H_2O at 200–600 °C and 250–350 atm for tens of days. H_2O may be enriched by K_2O to promote the synthesis procedure [33]. Although this is an effective approach and commonly used in the literature, its time-consuming process might be taken as one of its drawbacks. In structural modification method (IV), the composition of muscovite, is modified by an elemental substitution, e.g., fluorine–hydroxyl exchange in synthetic muscovite [34,35]. In addition to these techniques, Yuan and coauthors recently developed a sustainable and energy-saving approach for synthesizing nano-muscovite through a green chemical process by imitating the geochemical weathering process of k-feldspar [1]. This technique led to the production of muscovite with 20–45-nm thickness under hydrothermal conditions of 250 °C for 18–72 h by adjusting the ratio of $n(\text{H}^+)/n(\text{K}^+)$ in the presence of acetic acid ($\text{CH}_3\text{COOH} > 99.5\%$). By developing modern technologies, the demands for muscovite with specific sizes and qualities increase. Therefore, several studies have been conducted on its characterizations and applications. However, in recent years, the access to rich primary mineral resources and advances in the processing methods of these materials, especially the froth flotation process, have reduced the tendency to develop muscovite synthesis methods from other sources (i.e., secondary sources or individual starting materials). Moreover, although the discussed methods have given acceptable synthesis efficiency, the requirements of an extremely high temperature, pressure and process duration made them cost-intensive.

Given the significant reduction in high-quality mineral reserves, the search for efficient methods to extract, synthesize or recycle materials needed by industries from secondary sources is the simplest way to respect the rights of future generations and maintain their share of the existing primary reserves. For example, annually, millions of tons

of coal tailings are produced by coal beneficiation plants around the world and disposed in dumping sites. These coal residues can cause serious ecological and environmental problems due to potential contaminant transport issues. These problems can include the transportation of contaminants like heavy metals [36] and nano-minerals [37] from dumping sites, which leads to the contamination of groundwater and surface water sources. Additionally, other issues can be caused through the self-ignition of dry dumping sites and the pollution of surrounding environments with respect to the dispersion and emission of coal dust by wind. Regardless of their environmental impacts, these materials can be thought of as potential secondary resources, provided appropriate recycling methods are developed [38,39]. During the last decades, many attempts were made for the recycling and reusing of these materials. For example, the recovery of coal from coal waste and tailings has been considered by some small companies to produce low-energy briquette for domestic consumption, due to the high ash content [40]. The reuse of coal wastes in other fuel forms has also been considered by some researchers. For example, Opara et al. [41] investigated the production of biomethane from coal wastes and suggested that these materials can be used as a commercially viable source for the production of methane fuel. Zheng et al. [42] used a microbial consortium derived from sewage sludge for the production of methane from a coal waste sample and showed that coal waste can be partially digested into biomethane. Recently, Dmitrienko and Strizhak [43] showed that fine coal wastes in the form of coal–water slurry can yield better combustion properties. Vershinina and coworkers [44] evaluated the combustion characteristics of organic coal–water fuels produced by different oils and coal-processing wastes of different grades and reported that the development of coal–water fuel technology can be used as an efficient solution for coal waste recycling. Some researchers have investigated the potential applications of coal wastes in the manufacturing of construction products, such as cement [45], asphalt [46–48], brick [49,50] and concrete [51]. Despite the remarkable results of the above studies, their applicability has been limited due to large mineral-petrographic variations, fragmentations and low-energy characteristics. The noncombustible part of coal tailings, called ash, usually contains significant amounts of oxides of aluminum, iron and silicon and rare earth elements that can be used as raw materials in the synthesis of clay-type compounds. Referring to the literature indicates that the studies to date have mainly focused on the synthesis of zeolitic compounds from these materials [52–59], and to the authors' best knowledge, no study has been yet reported on the synthesis of muscovite from these materials. Therefore, in this paper, a simple open system method is introduced to synthesize muscovite from a lab ash produced from biotite-rich coal tailings. The crystalline properties of the synthesized samples were investigated through the common characterization techniques.

2. Materials and Methods

2.1. Material and its Preparation

A representative sample of coal tailings from Zarand Coal Washing Plant, Iran was used as the starting material for the synthesis process. Previous investigations showed that the noncombustible contents of these materials are rich in biotite [60]. Therefore, they can be considered as an abundant source for muscovite synthesis. Sampling was performed using a standard sampling scoop to prepare the representative sample for chemical analysis and synthesis experiments. The sampling program from the underflow stream of tailings thickener was scheduled for three days, with 2-h time steps at every work shift. Afterward, the samples were filtered, dried in an oven at 60 °C and mixed to obtain a 10-kg bulk sample.

The SEM image of the coal tailings is shown in Figure 1. As seen, the sample includes angular particles with no unusual surface patterns and excessive void spaces. In addition, as shown in Figure 1a, the samples are expected to have a fairly limited particle size distribution. Figure 1a demonstrates a large scale of the starting sample, while Figure

1b exhibits the surface microstructures with a reasonable contrast and resolution. The noncombustible contents of each sample were measured using a typical ash analysis procedure according to the American standard test sieve (ASTM D 3174-73), showing that the sample had 68.12% ash content. To produce the ash sample from the tailings, 60 samples of 1 g of coal tailings were milled and then heated up in a porcelain crucible at 850 °C for 8 h. These ash residues were used as the starting materials for synthesis studies. The chemical composition of the ash material was characterized using X-ray fluorescence (XRF, PW1480, Philips) and given in Table 1. As seen, SiO₂ and Al₂O₃ with respective magnitudes of 49.1% and 25.8% are the dominate components of the ash sample. In other words, alumina and silica oxide are present in major quantities; however, other minerals exist in trace amounts. This confirms the chemical analysis of the clay. It is worth mentioning that LOI is the loss on ignition in the head sample. Since the material studied here is taken from a coal tailing, it contains hydroxy compounds, which includes a high level of combined water as adsorbed and/or intracrystalline water. These components are shown later in the FTIR analysis.

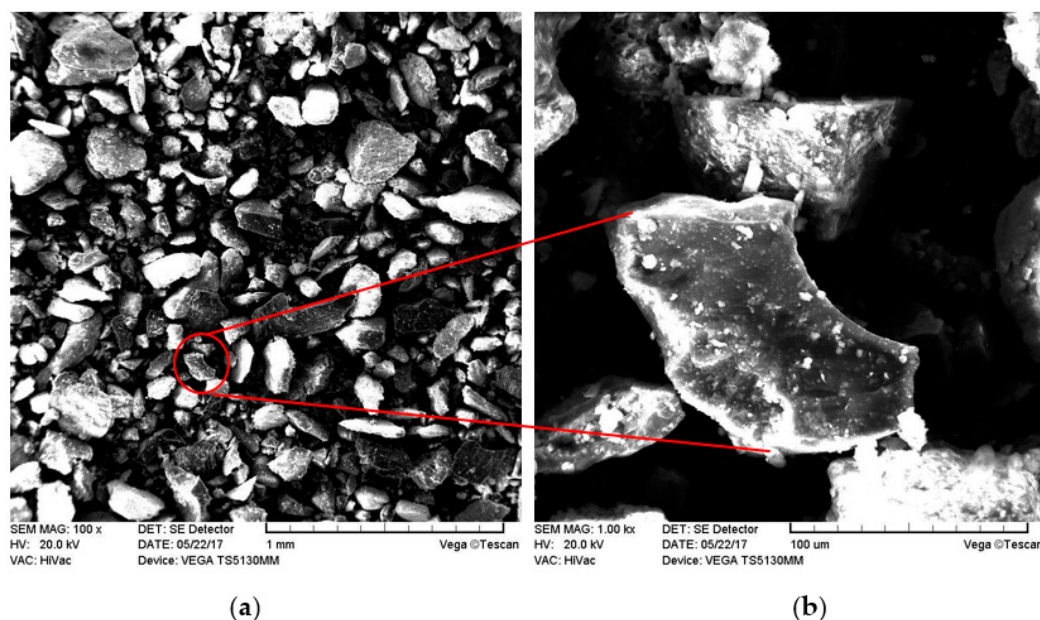


Figure 1. SEM image of the coal waste sample at (a) 100× and (b) 1000× magnification.

Table 1. Chemical composition of the noncombustible portion of the studied coal tailings.

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	L.O.I *
Content (wt%)	49.1	25.8	5.9	5.5	4.7	2.0	4.6	1.9	0.5

*LOI is the Loss on Ignition at 850 °C.

2.2. Synthesizing Approach

Referring to the chemical composition of biotite and muscovite, it is possible to transform biotite to muscovite by harsh oxidation. This can be achieved by a strong oxidant like hydrogen peroxide at the appropriate heating level. The procedure presented in this paper is based on a feasibility study in which a set of preliminary experiments were conducted to obtain the optimum conditions for the synthesis process as follows [60]. Initially, 20 g of the prepared lab ash was placed in a 500-mL glass beaker, and 250 mL volume of 35% H₂O₂ (Sadrashimi Chemical Co., Isfahan, Iran) was added at room temperature (25 ± 1 °C) with continuous stirring at 480 rpm. Then, the temperature was gradually raised to 80 °C. The synthesis was performed in an open system using a stirrer–heater equipped with a thermostat to adjust the temperature to 80 ± 2 °C, with continuous

stirring for 180 min. Finally, the slurry mixture was centrifuged at $10,000\times g$ for 20 min (Sigma 1-14, Osterode am Harz, Germany), and the precipitate was placed into a porcelain-evaporating basin and aged in an oven for 20 h at 95 °C.

2.3. Characterization

The phase determination and phase analysis were carried out by the X-ray diffraction (XRD, PHILIPS, X'pert-MPD system, Amsterdam, The Netherlands). In order to prepare the sample for XRD analysis, the ash product of the coal tailing was first ground into a fine powder ($<75\text{ }\mu\text{m}$) and then mixed with a suitable binding aid (a cellulose wax mixture combined with the sample in a proportion of 20% binder-to-sample). Afterwards, the mixture was pressed in a dye at 20 T to produce a homogeneous sample pellet. IR spectra were recorded on a Fourier-transform infrared spectrometer (FTIR, Bruker tensor 27, Berlin, Germany) with a RT-DLATGS detector. The morphology of the samples was determined by scanning electron microscopy (SEM) (Tescan Vega-II, Brno, Czech Republic). Seven-point analyses were performed on both the starting material and product.

The crystallite sizes of the samples were calculated using the Scherrer equation [61–63]. The crystallization system of the starting material and product was determined based on the X-ray method. Then, the lattice parameters were calculated in terms of the strongest high-angle reflections, so that the peaks were divided into $K_{\alpha 1}$ and $K_{\alpha 2}$ components at each reflection. The lattice parameters of the samples were calculated from the interception of the ordinate in the Nelson–Riley plot, i.e., a plot of the lattice parameter determined from individual reflections vs. $\cos 2\theta/\sin \theta$ [63].

3. Results and Discussion

3.1. XRD and SEM Analyzes

Figure 2a,b shows the XRD patterns of the starting material and synthesized product, respectively. The reference patterns are also shown in Figure A1 (Appendix A). By qualitatively comparing the results of both Figures 2 and A1, it was clear that the ash sample was a mixture of biotite and muscovite. Figure 2b illustrated that most of the diffraction peaks related to the biotite were converted into muscovite. These transformed phases obviously confirmed that the suggested process for the synthesis of muscovite from the biotite-rich lab ash was successful. To evaluate the conversion efficiency, the XRD patterns were quantitatively analyzed, and the muscovite content of the starting material and synthesized product were found to be 28.7% and 67.7%, respectively.

It should be noted that, since the main purpose of this study was to investigate the conditions of the conversion of biotite to muscovite, the presence of other minerals was not studied. Additionally, XRD patterns were analyzed only for the dominant and target phases—namely, biotite and muscovite. However, for the sake of clarity, the XRD results were also quantitatively analyzed and are presented in Table A1.

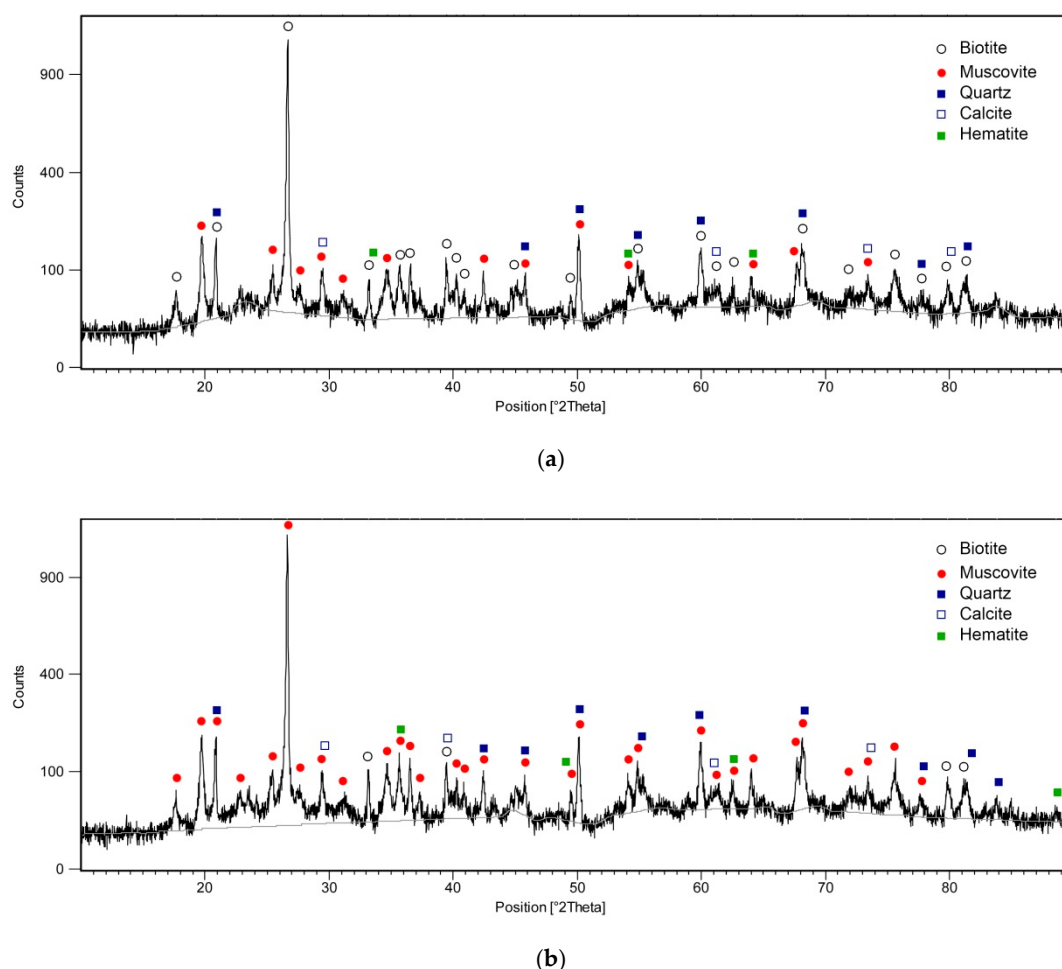


Figure 2. X-ray diffraction patterns of (a) the starting material and (b) synthesized muscovite.

Table 2 shows a comparison between the calculated and standard lattice and crystallographic parameters for biotite and muscovite. Cell axes in the monoclinic unit cell were of unequal lengths. Cell dimensions were $a = 5.34$, $b = 9.24$ and $c = 10.21$ Å for biotite and $a = 5.19$, $b = 9.01$ and $c = 20.06$ Å for muscovite. This manifested, because muscovite crystals faced in the direction of the c -axis larger than biotite. Therefore, it was expected that the synthesized product had larger crystals compared to the ash material.

Comparing the X-ray patterns of the starting material and treated product with the standard patterns showed that the starting material's peaks matched the ICDD reference pattern 01-080-1110 for biotite, and the product peaks matched the ICDD reference pattern 01-082-2450 for muscovite (Appendix A, Table A2).

In addition to high-angle reflections, the low-angle reflections were used to determine the lattice parameters of the samples. The K_{a1} and K_{a2} peaks for biotite and muscovite are given in the Appendix (Appendix A, Tables A2 and A3). Then, for each reflection angle, parameter d was determined using the Bragg equation below (Appendix A, Tables A4 and A5) [63]. These results were used for calculating the lattice parameters. After solving the equations, the lattice parameters were determined for the high reflections. Then, based on the Nelson–Riley equation and regression, the final lattice parameters were defined as shown in Table 3.

Table 2. Calculated and standard lattice parameters for biotite and muscovite.

Chemical Name	Lattice Parameters			
	a (Å)	b (Å)	c (Å)	β (degree)
Biotite (standard)	5.3370	9.2420	10.2110	100.1500
Biotite (starting material)	5.3343	9.2267	10.2560	100.0800
Muscovite (standard)	5.1940	9.0130	20.0640	95.8000
Muscovite (synthesized)	5.1767	8.9327	20.0786	96.8771

Referring to the standard amounts of the lattice parameters (Table 3), it revealed that the calculated lattice parameters for the starting material and product were significantly closed to the standard parameters. These results confirmed that the starting material was biotite, and the synthesized product was muscovite, with high crystallographic compliance. Table 3 also shows that the difference between the muscovite beta angle of the standard and product is one degree. In general, the process of analyzing and identifying the results of the XRD analysis is based on comparing the XRD pattern of the sample with the patterns that are available in the analysis software database. The result of this study is the selection of reference codes that are the most consistent with the sample pattern, and therefore, it is obvious that differences are observed in some crystallographic parameters.

The selected reference pattern may belong to a natural muscovite, whereas the muscovite sample in this study is a synthetic product with some defects in the crystallographic structure caused during the synthesis process. Therefore, the apparently significant difference in the beta angle of the reference and product muscovite can be attributed to the aforementioned reasons. The crystallographic information of some standard muscovite minerals available in the XRD Pattern Library is presented in Table 3. As can be seen, the beta angle difference in the standard samples can vary up to more than two units.

The mean crystallite sizes of the starting and treated samples were calculated to be 55 ± 0.09 nm and 87 ± 0.23 nm, respectively. These values verified the growth of the product's crystals, as observed in the SEM images. Both the crystallite size and morphology shown in Figure 2b verify a potential application of the product as an additive material in different industries, such as the coating paint of automobile industries, mica-paper fabrication and mica-glass ceramic [1].

Table 3. Crystallographic parameters of some muscovite samples available in the X-ray diffraction (XRD) database.

Reference Code	Lattice Parameters			
	a (Å)	b (Å)	c (Å)	β (degree)
01-082-2450	5.1940	9.0130	20.0640	95.8000
01-082-2451	5.1510	8.9310	19.3990	95.8000
00-025-0649	9.1120	5.2600	20.0330	97.8700
01-085-2147	5.1740	8.9750	19.7700	95.2000

Figure 3a,b represents the SEM images of the starting material and synthesized product, respectively. The SEM photographs revealed the differences among the biotite and muscovite structures. Biotite was crystallized in a monoclinic system with tabular-to-prismatic crystals with an obvious pinacoid termination. It has four prism faces and two pinacoid faces to form a pseudo-hexagonal crystal (designated by "H"), which can be observed in Figure 3a. In contrast, muscovite was crystallized in a monoclinic system with amorphous pseudo-crystals. This conclusion is found to be in line with the results addressed in the literature [2,64]. A comparison between Figure 3a,b clearly shows that the pseudo-hexagonal crystals were disappeared after the synthesis to amorphous pseudo-crystals. This crystalline conversion can be considered as evidence of biotite-to-muscovite conversion.

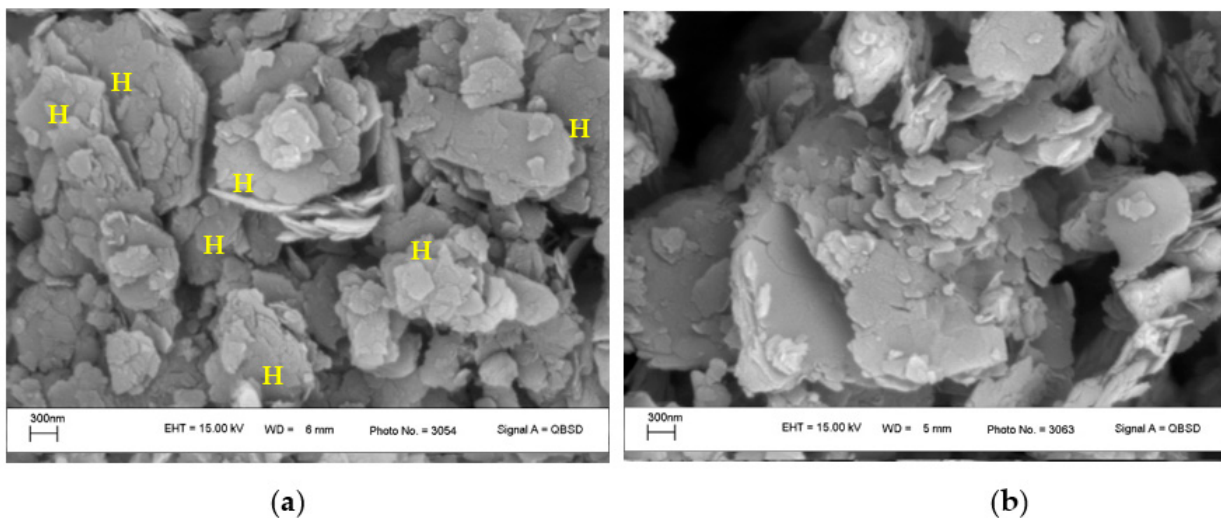


Figure 3. SEM images of (a) the starting material and (b) treated product (synthesized muscovite). H designates pseudo-hexagonal crystals. EHT = Electron High Tension; WD = Working Distance; QBSD = Back-Scattered Detector (Quadranten Rückstreu-Elektronen Detektor).

3.2. Infrared Spectroscopy Results

Figure 4a,b exhibits the FTIR spectrum of the starting material and treated product, respectively. Since both samples were mixtures of biotite and muscovite, it was difficult to distinguish the peaks corresponding to each mineral. However, these spectra were similar to those reported in the literature [26,65–69]. The band positions for the starting material and synthesized product are given in Table 4. The hydrous nature was confirmed by the FTIR analysis showing the presence of —O—H bonds at 3451.32 and 3450.89 cm^{-1} for the starting material and synthesis product, respectively. Further, the Si—O stretching vibrations were observed at 1073.93 , 560.46 and 483.61 cm^{-1} for the product representing the presence of quartz, as can be confirmed by Table A1 and addressed by Marel and Bentelspacher [70] in the literature. Si—O—Al stretching vibrations at 707.58 and 560.46 cm^{-1} correspond to the possibility of the presence of calcite, as given in Table A1. In this context, Gadsen [71] identified a band at 693.4 cm^{-1} for calcite, which is in the range of our findings. At the wavelengths of 1077.86 and 1073.93 cm^{-1} , the peak of the starting material was relatively sharper than that of the synthesized one, most likely due to its higher content of biotite and/or quartz [72]. As can be seen in Table 4, this peak is dedicated to the Si—O stretching vibrations that identify quartz and include 3.9 wt% and 2.7% of the starting and produced materials. In addition, the higher sharpness of the peaks in Figure 4 indicated that the crystals contained in the starting material were more regular than the crystals of the treated sample [73,74]. In this regard, the SEM photographs also showed a clear growth in the dimensions of the muscovite crystals.

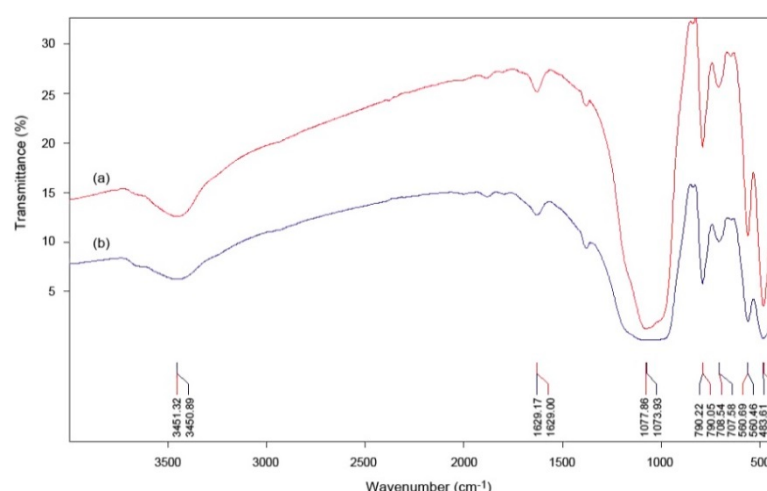


Figure 4. A comparative demonstration of the Fourier-transform (FT) infrared spectra of (a) the starting material and (b) treated product (synthesized muscovite).

Table 4. The infrared (IR) absorption bands for the starting material and synthesized product.

Band (cm ⁻¹)		Assignment(s)
Starting Material	Synthesized Product	
3451.32	3450.89	–O–H
1629.00	1629.17	H–O–H
1077.86	1073.93	Si–O
790.05	790.22	Al–O–Al
708.54	707.58	Si–O–Al
560.69	560.46	Si–O; Si–O–Al
482.07	483.61	Si–O; Si–O–Fe

4. Conclusions

The present study proposes a potential method for synthesizing muscovite from an ash sample produced from biotite-rich coal tailings using an easy and open system process. In contrary with the other techniques, this approach is a safer and, more importantly, shorter process. The synthesized muscovite properties and efficiency of the conversion process were evaluated by the XRD, SEM and FTIR analyses. The XRD pattern of the synthetic product proved that the conversion was successfully achieved. The conversion also appeared in the FTIR and SEM results through crystalline growth and change from biotite's pseudo-hexagonal crystals to muscovite's amorphous pseudo-crystals. Additionally, the crystallography study and lattice parameter calculations confirmed the analytical results. It was found that the mean crystallite size of the starting material grew from 55 ± 0.09 nm to 87 ± 0.23 nm in the case of the synthesized product. These results are in agreement with those observed in the SEM images. From the findings in this study, the proposed method seems to be a promising and potential bedrock process. For future investigations, we believe this process may need further optimization and detailed characterizations. Moreover, the descriptions of the reactions involved in the phase changes from the thermodynamic and kinetic point of views can be considered as future studies.

Author Contributions: Conceptualization: H.K. and V.S.; methodology: H.K. and V.S.; original draft preparation: H.K. and V.S.; writing—reviewing and editing: H.K., V.S., A.H., T.N. and A.S.; investigation: H.K. and V.S. and visualization and supervision: H.K. and V.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Experimental and reference XRD patterns.

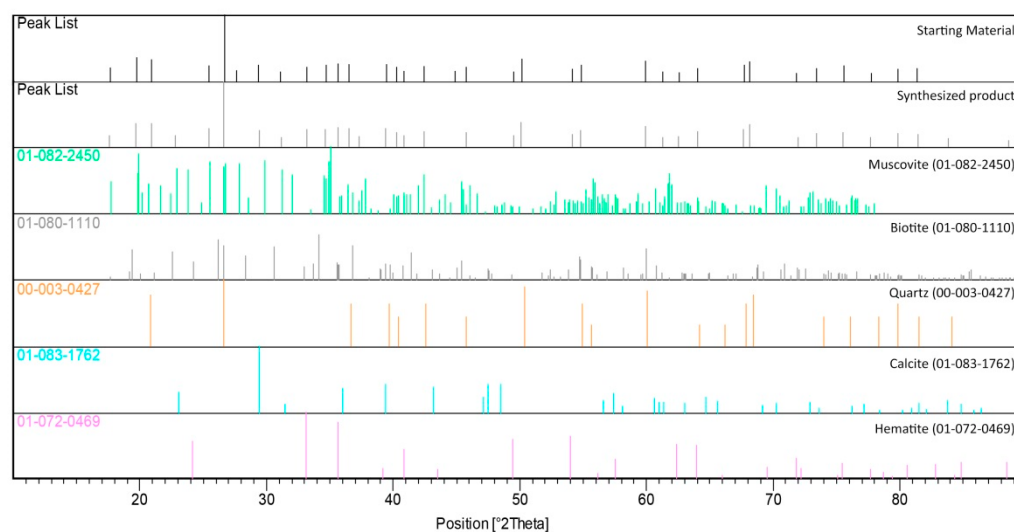


Figure A1. Experimental XRD patterns vs. reference patterns of the starting material and synthesized product.

Table A1. Major and minor phases in the starting material and synthesized product.

Phase	Major Phases (wt%)		Minor Phases (wt%)		
Sample	Biotite	Muscovite	Quartz	Calcite	Hematite
Starting material	64.4	28.7	3.9	2.0	1.0
Product	27.6	67.7	2.7	1.0	1.0

Crystallography study of both the starting material (Table A2) and synthesized product (Table A3).

Table A2. $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks for the reflections of the starting material.

2θ (degree)	$d(\text{\AA})$	hkl	$K_{\alpha 1}$ (degree)	$K_{\alpha 2}$ (degree)
39.4824	2.282	220	39.448	39.550
44.8831	2.01953	005	44.844	44.961
71.8665	1.31372	064	71.797	72.003
75.5809	1.25811	262	75.507	75.728
77.7888	1.22783	172	77.712	77.942
79.8642	1.20106	-405	79.785	80.023
81.4022	1.18124	-228	81.402	81.647

Table A3. K α_1 and K α_2 peaks for the reflections of the product.

2 θ (degree)	d (Å)	hkl	K α_1 (degree)	K α_2 (degree)
34.6530	2.58863	200	34.623	34.712
40.2683	2.23967	220	40.233	40.338
50.1131	1.82034	0210	50.069	50.202
63.9994	1.45483	0213	63.940	64.118
68.1187	1.37655	−337	68.054	68.247
71.9970	1.31164	−1115	71.928	72.135
73.4356	1.28946	068	73.365	73.577
77.7092	1.22889	−1116	77.633	77.862

Table A4. Calculations of the d-spacing based on the Braggs equation for the starting material.

2 θ	θ (radian)	λ	Sin θ	Sin2 θ	$\lambda_{\alpha 1^2} / \lambda_{\alpha 2^2}$	Sin2 θ	h	k	l	4(Sin2 θ)/ λ^2
39.448	0.344249	k α_1	0.33749	0.1138992	0.995048962	0.1138992	2	2	0	0.191965649
39.55	0.345139	k α_2	0.338327	0.1144654	0.995048962	0.1138987	2	2	0	0.191964722
44.844	0.391338	k α_1	0.381425	0.1454853	0.995048962	0.1454853	0	0	5	0.245200787
44.961	0.392359	k α_2	0.382369	0.146206	0.995048962	0.1454822	0	0	5	0.245195507
71.797	0.626547	k α_1	0.586351	0.3438077	0.995048962	0.3438077	0	6	4	0.579453137
72.003	0.628345	k α_2	0.587806	0.3455164	0.995048962	0.3438057	0	6	4	0.579449878
75.507	0.658923	k α_1	0.612266	0.3748691	0.995048962	0.3748691	2	6	2	0.631804109
75.728	0.660851	k α_2	0.613789	0.3767373	0.995048962	0.374872	2	6	2	0.631809002
77.712	0.678165	k α_1	0.627365	0.3935871	0.995048962	0.3935871	1	7	2	0.663351385
77.942	0.680172	k α_2	0.628927	0.3955491	0.995048962	0.3935907	1	7	2	0.663357484
79.785	0.696255	k α_1	0.641349	0.4113288	0.995048962	0.4113288	−4	0	5	0.693253191
80.023	0.698332	k α_2	0.642941	0.4133736	0.995048962	0.411327	−4	0	5	0.693250075
81.402	0.710366	k α_1	0.652112	0.4252496	0.995048962	0.4252496	−2	2	8	0.716715267
81.647	0.712504	k α_2	0.653731	0.4273643	0.995048962	0.4252484	−2	2	8	0.716713211

Table A5. Calculations of the d-spacing based on the Braggs equation for the product.

2 θ	θ (radian)	λ	Sin θ	Sin2 θ	$\lambda_{\alpha 1^2} / \lambda_{\alpha 2^2}$	Sin2 θ	h	k	l	4(Sin2 θ)/ λ^2
34.623	0.302143	k α_1	0.297566501	0.0885458	0.995048962	0.0885458	2	2	0	0.149227687
34.712	0.302919	k α_2	0.2983079	0.0889876	0.995048962	0.088547	2	2	0	0.149229709
40.233	0.351099	k α_1	0.34393012	0.1182879	0.995048962	0.1182879	0	0	5	0.199352531
40.338	0.352015	k α_2	0.344790375	0.1188804	0.995048962	0.1182918	0	0	5	0.199359093
50.069	0.436934	k α_1	0.423163908	0.1790677	0.995048962	0.1790677	0	2	10	0.30178564
50.202	0.438095	k α_2	0.424215228	0.1799586	0.995048962	0.1790676	0	2	10	0.301785446
63.940	0.557982	k α_1	0.529475155	0.2803439	0.995048962	0.2803439	0	2	13	0.472468114
64.118	0.559567	k α_2	0.530792256	0.2817404	0.995048962	0.2803455	0	2	13	0.472470763
68.054	0.593883	k α_1	0.559583516	0.3131337	0.995048962	0.3131337	−3	3	7	0.527772924
68.247	0.595567	k α_2	0.560978578	0.314697	0.995048962	0.3131389	−3	3	7	0.527733796 5
71.928	0.62769	k α_1	0.587276816	0.3448941	0.995048962	0.3448941	−1	1	15	0.581255459
72.135	0.629497	k α_2	0.588737945	0.3466124	0.995048962	0.3448963	−1	1	15	0.581259197
73.365	0.64023	k α_1	0.597380231	0.35686367	0.995048962	0.3568631	0	6	8	0.601427143
73.577	0.64208	k α_2	0.598862869	0.3586367	0.995048962	0.3568611	0	6	8	0.601423725
77.633	0.677476	k α_1	0.626828219	0.3929136	0.995048962	0.3929136	−1	1	16	0.662183585
77.862	0.679474	k α_2	0.628384036	0.3948665	0.995048962	0.3929115	−1	1	16	0.662180015

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